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A MANUAL OF DYEING.

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MANUAL OF DYEING:

FOR THE USE OF PRACTICAL DYERS, MANUFACTURERS, STUDENTS, AND ALL INTERESTED IN THE ART OF DYEING.

BY

EDMUND KNECHT,
PH.D. (ZÜRICH), M.SC.TECH (MANCHESTER), F.I.C.,
PROFESSOR OF TECHNOLOGICAL CHEMISTRY, VICTORIA UNIVERSITY OF MANCHESTER; AND HEAD OF THE CHEMICAL DEPT., MUNICIPAL SCHOOL OF TECHNOLOGY, MANCHESTER, EXAMINER IN DYEING TO THE CITY AND GUILDS OF LONDON INSTITUTE; EDITOR OF *The Journal of the Society of Dyers and Colourists*;

CHRISTOPHER RAWSON,
F.I.C., F.C.S.,
ANALYTICAL AND CONSULTING CHEMIST; SOME TIME HEAD OF THE CHEMISTRY AND DYEING DEPT., TECHNICAL COLLEGE, BRADFORD; VICE-PRESIDENT OF THE SOCIETY OF DYERS AND COLOURISTS;

AND

RICHARD LOEWENTHAL, PH.D. (MUNICH),
TECHNICAL CHEMIST AND COLOURIST, SOMETIME HEAD OF THE DYEING AND FINISHING DEPARTMENT OF THE ROYAL WEAVING SCHOOL, COTTBUS.

Ninth Edition.
(Reprinted)

COMPLETE IN TWO VOLUMES WITH NUMEROUS ILLUSTRATIONS, AND FIVE PLATES.

VOL. I.

LONDON:
CHARLES GRIFFIN AND COMPANY, LIMITED;
42 DRURY LANE, W.C.2.
1941

Printed in Great Britain
by Bell & Bain, Limited, Glasgow.

PUBLISHERS' NOTE TO NINTH EDITION.

THIS comprehensive standard work has attained pre-eminence in all industrial centres of the textile trades both in this country and abroad. It deals authoritatively with a wide range of subjects, and the constant demand for copies is the best evidence of its continued usefulness.

PREFACE TO THE SECOND EDITION.

ALTHOUGH the general arrangement of subjects has not been materially altered in the present edition, the great changes which have taken place in the practice of dyeing since the issue of the first edition—due to the introduction of new methods, new products, and new machinery—have necessitated the re-writing of large portions of the work, the addition of much new matter, and the omission or curtailment of certain parts of the original text. The illustrations of fibres and machinery have been almost entirely replaced by new ones, while the empirical tables for the identification of dyestuffs on the fibre, given at the end of Vol. II. of the first edition, have been replaced by the more rational systematic tables of Prof. A. G. Green. After careful consideration, it was decided not to re-issue the dyed patterns which constituted Vol. III. of the first edition, the authors being of the opinion that they were not of sufficient interest to the practical dyer.

A special feature of the new edition will be found in the numerous references given in footnotes to current English and Foreign literature, but more particularly to the *Journal of the Society of Dyers and Colourists* and the *Journal of the Society of Chemical Industry*. Although the number of original publications referred to in the former is small compared to that of the abstracts, no apology is offered for not in all cases giving the original reference. The English abstracts will, in most cases, give the necessary information, but if more is required, the original source is invariably given in the Journal.

No efforts have been spared to bring the present edition up to date, but the authors are, nevertheless, conscious of the fact that, in consequence of the time that has elapsed since the first sheets went to press, and the rapid progress which is continually being made in this branch of applied chemistry, it has not been possible to include the results of some of the more recent publications and researches.

December, 1909. THE AUTHORS.

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A MANUAL OF DYEING.

PART I.

INTRODUCTION.

In its broadest sense, *dyeing* is the operation or series of operations by means of which uniform colour, of a more or less permanent character, is produced in the substance of objects. The term *tinting* is literally the same as dyeing, but is only applied to the production of very light or delicate shades. *Staining* has a similar meaning, but, on the large scale, the use of the term is almost entirely restricted to the production of coloured paper. In these processes the colour is presented to the object in a dissolved condition, and in being taken up permeates more or less uniformly the whole mass of the substance. In *painting*, the colour is imparted to the object by covering the surface with a coloured body or pigment, which does not necessarily penetrate into the substance; the coloured bodies employed for the purpose are usually insoluble, and are fixed by means of adhesives. In textile *printing*, the colour is produced on portions only of the material, and in such a manner as to produce a definite pattern, but in other respects printing is, in principle, closely allied to dyeing.

The dyeing of textiles, either in the woven fabric or in the intermediate stages of manufacture, by far exceeds in importance the dyeing of other objects, such as leather, feathers, straw, horn, ivory, bone, wood, &c.; the former subject only will be dealt with in this work. But even if the scope of the work be restricted to this industry alone, it would be impossible to go into the details of every speciality. Indeed, this is not its object, the main aim being to lay down broad principles, and to show how science, especially Chemistry, underlies most operations in dyeing, and may be usefully applied in detecting the origin of faults, in improving existing methods, or in working out new methods or effects. That a knowledge of chemistry is most useful to the dyer will scarcely be doubted; but the smaller his knowledge, the more circumspect should he be in making use of it. Chemistry has done a great deal towards the furtherance of the dyeing industry. During the last two decades it has almost revolutionised certain portions of it, and it may be safely predicted that in the future it will do much more than has been the case in the past.

FIBRES, COLOURING MATTERS, AND MORDANTS.

In any dyeing process, the two main factors which determine the mode of working are—first, the character of the fibre to be dyed; and secondly, the properties of the dyestuff or dyestuffs employed to produce the desired colour.

In many dyeing processes, however, the dyestuff cannot be employed alone, the colour being only obtainable with the aid of so-called mordants.

Fibres.—As will be seen in detail further on, the fibres which claim the attention of the dyer are mainly of two distinct kinds, viz.:—(1) The vegetable fibres (cotton, linen, &c.); and (2) the animal fibres (wool and silk). These materials differ essentially from each other in their origin and in their chemical composition and properties; they also behave very differently in dyeing. In the following statements we may assume cotton to represent the vegetable fibres as a class, and wool the animal fibres. If two swatches or fents,* composed of woollen and cotton material respectively, are immersed in a boiling, but very dilute, solution of Benzopurpurin, and kept stirred in the solution for some time, it will be noticed on taking them out and rinsing that both fibres are dyed about the same shade of red. If the experiment be repeated, using New coccin in place of Benzopurpurin, and adding a few drops of dilute sulphuric acid to the bath, it will be seen on rinsing the swatches that the wool is dyed a full and brilliant shade of red, while the cotton is only tinged.

Further, if cotton and wool are heated simultaneously in a very weak solution of a basic dye, such as Crystal violet, it will be seen that the wool is dyed a full shade, while the cotton is only tinged. By previously steeping the cotton in a solution of tannic acid, however, it acquires the property of attracting the dyestuff, in consequence of the fibre having absorbed some of the tannic acid, which latter yields with the basic dyes insoluble coloured precipitates or lakes.

But if cotton and wool be boiled in water containing a small quantity of a dyestuff like Alizarin, neither fibre is dyed in the true sense. They will both be tinged a nondescript colour, which is more or less completely removed by washing. If, however, the wool be previously boiled in a weak solution of alum, with a little tartar added, and the cotton impregnated with a solution of aluminium acetate, dried slowly and passed through a bath of arseniate of soda, both fibres are said to have been mordanted; they will then be dyed on boiling in the Alizarin full shades of red, which cannot be removed by washing or even soaping.

From these few examples it will be clear that not only do the fibres differ very materially from each other in their affinity for colouring matters, but that the various classes of dyestuffs require totally different modes of application, according to the character of the dyestuff and that of the fibre on which they are to be dyed.

Colouring Matters.—The large number of *dyestuffs* or *colouring matters* which are at the disposal of the dyer are principally of organic origin; some few are also derived from the mineral kingdom. The oldest classification of these various substances is that of Bancroft, who divides them in his *Treatise on Permanent Colours* (published over 100 years ago) into *Substantive dyes* and *Adjective dyes*. According to this classification, he regarded all dyes as Substantive which, like indigo, orchil, turmeric, &c., will dye the textile fibres directly; the dyestuffs, of which Congo-red, New coccin, and Crystal violet are representatives, would also belong to this class. Adjective dyes will only dye material mordanted with a metallic salt or hydroxide, or with the addition of a metallic salt or hydroxide to the dye-bath—such are, for instance, logwood, madder, cochineal, fustic. In the pure state the adjective dyes are generally only slightly coloured, and, when used alone in dyeing, they give rise to worthless results. But when used in conjunction with metallic mordants, such as the salts of iron, alumina, chromium, or tin, intensely coloured insoluble compounds—so called *lakes*—are produced in the substance of the fibre, which thus becomes dyed. Similar lakes can be produced without the presence of

* A swatch or fent is a small sample of material cut or torn from the piece.

the fibre by adding the metallic salts either to the aqueous or to the slightly alkaline solution of the adjective colouring matter.

Bancroft's classification is still in general use.

Nietzki's classification * of the colouring matters into *direct dyes* and *mordant dyes* (that is, into such as will dye directly, and such as will only dye with the intervention of a mordant) is practically the same as Bancroft's.

Hummel † classifies the colouring matters as *monogenetic* and *polygenetic*. Monogenetic are such as are only capable of yielding one colour, whatever mordant may have been used on the material, either before or during the dyeing operation. Magenta, orchil, indigo, Picric acid, Methyl green, may serve as examples of this class. Polygenetic colours are such as are capable of producing totally different colours according to the mordant employed. Examples of this class are logwood, Alizarin, fustic, and cochineal. The term *autogenetic* colours employed by Scheurer is practically synonymous with Hummel's monogenetic class.

The direct dyes may be further classified as *direct dyes for cotton, direct dyes for wool and silk: acid dyes, and basic dyes.* The direct dyes for cotton will dye all textile fibres; the acid dyes are mostly only applicable to wool and silk; while the basic dyes have a direct affinity for wool and silk, but not for cotton. To be dyed with the basic dyes, the latter must be first mordanted with tannic acid or an oil mordant. In some cases the mordant dyes may serve as fixing agents for the basic dyes on cotton. Thus, Magenta is readily fixed on cotton which has been previously mordanted with alumina and dyed with Alizarin. Cotton previously dyed with a direct colour, such as Chrysamine, or a sulphide colour like Immedial blue, is also rendered capable of taking up basic dyes.

Generally speaking, the mordant colours can be fixed equally well on either animal or vegetable fibre, and from the point of view of the dyer, there are no grounds for a further subdivision of this class.

Many important colours which are produced on and in the fibre by special chemical processes, such as oxidation, as in the case of Aniline black; by combination, as in the case of the insoluble azo dyes produced on the fibre (Paranitraniline red, Primuline red, &c.); or by condensation, as in the case of Nitrosoblue, do not, strictly speaking, come within the scope of any of the above classifications. They are frequently classed as substantive, direct, or monogenetic colours, because they are produced without a mordant, but we prefer to class them under a separate heading—viz., that of *Developed colours.*

Pigment colours are insoluble coloured substances like vermilion, ultramarine, or lamp black, which find little or no application in dyeing. They are used in calico-printing, and are usually fixed by means of albumen.

The colouring matters are also sometimes classified, according to their origin, as (1) natural colouring matters, (2) artificial colouring matters (aniline or coal-tar colours), and (3) mineral colours. Although it may be urged that this classification is not by any means a scientific one, inasmuch as there exists no fundamental difference between the chemical constitution of the natural and the artificial organic dyestuffs, it has been decided to adhere to it in the present edition, as it is not considered that a grouping of the colouring matters according to strictly chemical principles would, as yet, be of advantage from the dyer's point of view. After all, there is a very essential difference in the forms in which the two different classes of products are supplied to the dyer, and which materially influences their application. The artificial colouring matters are products which are either chemically pure, or contain, at most, harmless additions; but can always be obtained of one and the same quality.

* R. Nietzki, *Färber Ztg.*, 1889-90, p. 8. † *The Dyeing of Textile Fabrics*, p. 147.

The natural colouring matters, however, with the exception of indigo, usually contain their active constituent in very small and varying quantity. and special treatment is, in most cases, required for its extraction.

Relation of Colour to Chemical Constitution.—There undoubtedly exists a close relationship between the dyeing properties and the chemical properties of colouring matters; this has, in fact, been proved to be the case with most colouring matters, the constitution of which has been established. Græbe and Liebermann * were the first to express the view that the dyeing properties of organic compounds depend upon an intimate connection between oxygen and nitrogen atoms, and that by weakening such connection by the introduction of hydrogen atoms the dyeing properties of such compounds were destroyed. The compounds thus produced are known as leuco-compounds.

The views of these chemists were considerably enlarged by the investigations of O. N. Witt.† According to him, the dyeing properties of organic compounds are determined on the one hand by "colour-bearing," and on the other by "salt-forming" groups of atoms. The colour-bearing groups, which he terms *chromophors*, consist, according to our present knowledge, of two or more atoms of one or more of the following four elements—carbon, oxygen, nitrogen, and sulphur. The chromophor alone is not capable of changing a simple compound (hydrocarbon) into a colouring matter; it is necessary, in order that this may be accomplished, that a salt-forming or *auxochromous* group or groups (of which the amido-NH_2 and hydroxyl-OH groups are of predominant importance) should also be present in the molecule. Compounds which contain a chromophor, but not an auxochromous group, and though coloured are not colouring matters, he terms *chromogenes*.

Witt's theory has led to important practical results, by which, however, the colour manufacturer has benefitted directly more than the dyer. It will be referred to again under the heading *Artificial Colouring Matters*.

THE DYEING PROCESS.

In their natural condition, the textile fibres are either colourless or they possess a colour which meets with little or no approval. A very large proportion of the total manufactured output (especially of cotton and linen) comes into the market undyed and usually bleached, but in the rest of the cases the dyer and printer are called upon, in order to meet the requirements of the public, to produce any shade or pattern which they may be asked for.

The fibres may be dyed either in the loose state (*i.e.*, without having undergone any mechanical treatment), in the intermediate stages of manufacture (sliver, slubbing, &c.), or in the yarn or piece. Piece dyeing is the most economical and convenient, and, consequently, the most used. Yarn dyeing comes next in importance, and, last, the dyeing of the fibres in the raw or loose state, which accounts for the smallest proportion of the total output.

Mordants.—The name is derived from the French word *mordre* (to bite or corrode), because the early French dyers believed that the utility of the metallic salts they employed consisted in their corrosive nature; it was believed that these substances opened the pores of the textile fibres and thus rendered them more capable of absorbing the dyestuffs. At a later period it was recognised that the so-called mordants entered into a chemical combination with the dyestuffs and formed insoluble compounds, or "colour lakes"; hence these substances were considered principally as fixing agents for the dyestuffs. In many cases this is true—*i.e.*, where a dyestuff dyes without the aid of mordants, and becomes simply faster to washing and milling by the applica-

* *Berl. Ber.*, 1868, p. 106. † *Ibid.*, 1876, p. 522.

tion of the mordant. In most cases, however, the mordant is an essential constituent of the colour, as without it no colour at all or only a worthless shade is produced. We consider as mordants substances which, partly or wholly, combine with the dyestuffs to form definite compounds in the fibre, thus distinguishing them from those compounds which take part in the dyeing process without entering into the composition of the ultimate colour.

Chemically there is no essential difference between such chemical compounds and mordants; hence they will be described together in Part V. without being formally separated, but their applications in mordanting and dyeing will be dealt with specially in subsequent paragraphs.

The mordants may be classified as *acid* and *basic* mordants. The acid mordants, of which the tannins and the oil (fatty acid compounds) mordants are the most important, serve for the fixation of basic dyestuffs and metallic oxides; they are often used for fixing basic mordants on the fibre, which latter then act as the true mordants in dyeing. Their chief application is in the dyeing of cotton and linen, and in silk weighting.

The basic mordants contain the hydrated oxides of the heavy metals as their active constituents; of this class the most important are compounds (salts) of aluminium, iron, chromium, copper, and tin. In accordance with their basic character, these mordants serve for the fixation of acid or phenol-like dyestuffs.

As far back as the eighteenth century it was observed that for the dyeing of cotton with madder and alumina mordants calcareous water was necessary; the influence of lime in water used for dyeing with other mordants and dyestuffs was also noticed. In 1882, Horace Koechlin, in a communication to the Société Industrielle de Mulhouse, pointed out that certain colouring matters could be more readily fixed on cotton by means of *double mordants* (containing two metals) than by simple ones. Such double mordants were prepared by mixing aqueous solutions of acetate of alumina, or acetate of chrome with either acetate of lime or acetate of magnesia. He showed that calico prepared with such mordants could be dyed with Phloxin, Scarlet 3 R, and other colouring matters. Some years later he recommended for the fixation of St. Denis red a treble mordant consisting of alumina, magnesia, and oxide of zinc, and showed that this treble mordant was also capable of fixing other azo dyes yielding bright shades which were comparatively fast to soap.*

Following up this subject more closely from a scientific point of view, Prudhomme,† taking as his starting point Vauquelin's observation that alumina precipitated in presence of magnesia is insoluble in caustic alkalies, discovered that, besides magnesia, other metals possess the property of producing compounds with alumina insoluble in alkalies, which are useful as mordants; and further, that other metallic oxides which are soluble in alkalies are capable of yielding, like alumina, insoluble compounds of this character or *compound mordants.* Nickel and cobalt salts, for instance, act better than magnesium salts in rendering the precipitated alumina insoluble in caustic soda, while tin and zinc salts form with each other a compound mordant which is also insoluble in caustic soda. Prudhomme maintains that in cotton dyeing compound mordants are invariably produced, either intentionally or accidentally, on the fibre, and that there is no such thing as a simple mordant. The best mordants consist of compounds of sesquioxides, like alumina, chromic oxide or ferric oxide, with monoxides, like lime, magnesia, or zinc oxides. In some cases treble mordants give even better results. Thus iron fixed with arseniate of soda or phosphate of soda gives better results with lime or magnesia than without these oxides.

According to J. Thom, the mordants exhibit an elective affinity for

* H. Koechlin, *Bull. de la Soc. Ind. de Mulhouse*, 1882, p. 226; *ibid.*, 1889, April.
† *Bull. de Mulhouse*, 1891, pp. 39 and 217.

colouring matter—*i.e.*, they possess a greater affinity for some colouring matters than for others. Thus, if a piece of cloth mordanted with alumina be boiled in a decoction of quercitron bark, it is dyed yellow. If the same sample be now heated in a decoction of logwood, the colouring matter of the quercitron is displaced by that of the logwood and the colour of the cloth changes from yellow to purple. If the sample be now heated with madder, the colour changes from purple to red. The inference is that of the three colouring matters mentioned, madder (Alizarin) has the greatest affinity for alumina. On the other hand, it has been shown by Knecht * that a similar phenomenon is observed with regard to metallic mordants, inasmuch as the dark slate-coloured tannate of iron is rapidly changed to the orange-coloured tannate of titanium by immersing the fibre in a solution of titanic chloride.

The dyeing and mordanting of textile fibres are almost invariably effected by immersing the material to be dyed in the solution of the dye or mordant in cold or hot water, and either keeping it moved in the dye solution or causing the latter to circulate through the material until the desired shade is obtained. In rare cases other solvents, such as benzene or alcohol, are employed in place of water (dry dyeing). In any case the solvent simply acts as a distributing agent for the dye, causing it to permeate more or less uniformly every part of the material. Exceptions are found to this in the case of *spray dyeing*, in which a fine spray of the dissolved dyestuff is blown on to the piece, and in colouring one face only of the cloth by printing it with a thickened colour in a printing machine.

Dyeing is effected in *neutral*, *acid*, or *alkaline* solution, according to the material to be dyed and the dyestuff employed. Cotton is generally dyed, neutral or alkaline, not often in an acid bath. Wool is rarely dyed in an alkaline bath, but generally either acid or neutral. Worsteds dyed in an acid bath "finish" better than when dyed neutral or alkaline. Silk is generally dyed with basic colours in boiled-off liquor—*i.e.*, in an alkaline bath. In the black-dyeing of silk with logwood the bath is usually rendered alkaline by the addition of soap. Many colours are only applicable to silk in an acid bath, and for these an acidulated bath of boiled-off liquor is frequently employed.

In dyeing it frequently happens that the whole of the colouring matter is taken up by the fibres, leaving the bath colourless or only faintly tinged. Such colouring matters are said to *exhaust* well, and the phenomenon is particularly noticeable with many mordant colours, basic colours dyed on tanned cotton, and acid colours on wool. On the other hand, it is noticed that many colouring matters exhaust very imperfectly, leaving, even under favourable conditions, a large proportion of colour in the bath. This applies especially to the direct colours and sulphide colours when dyed on cotton.

The *temperature* employed in dyeing varies according to the fibre to be dyed and the dyestuff employed. Thus, cotton may be dyed cold (indigo, chrome, yellow, &c.), or at the boil (logwood blacks, direct colours). For wool, a boiling temperature is almost invariably required, while for silk it is found preferable to use a moderate heat in order not to affect the gloss and feel of the fibre.

The *amount of water* employed for a given weight of material to be dyed also varies considerably according to the character of the fibre, the dyestuff employed, and the stage of manufacture in which the dyer receives it. Generally speaking, cotton is dyed in 10 to 30 times its weight, wool in 50 to 100 times its weight of water, silk occupying an intermediate position. With colours which do not exhaust well, the use of as little water as possible in the dye-bath is not only economical but in certain cases (*e.g.*, direct blacks

* *Journ. Soc. Dyers and Col.*, 1904, p. 98.

and dyed Aniline black on cotton) a necessity. On the other hand, a concentrated dye-bath does not always give the best results. Thus, in the dyeing of Alizarin red on cotton, experience has shown that plenty of water should be employed. In silk dyeing the amount of water used in the dye-bath is somewhat greater than what is used for cotton. In any case, the volume of water required will also depend to a great extent upon whether the material is in the loose, spun, or woven state.

The standard *time* allowed for a dyeing operation in the laboratory is usually one hour, and this is in accordance with the majority of operations in the works. In practice, however, the time may vary enormously—viz., from a few minutes (in certain applications of the direct and of the sulphide colours on cotton) to three hours (certain Alizarin colours on wool).

The object of *mordanting*, an operation which, as a rule, precedes the dyeing, is to fix on the material to be dyed a *mordant*, generally a metallic hydrate or basic salt which is capable of forming a colour-lake with an adjective colouring matter. In mordanting wool and silk, practically the same operations are employed as in dyeing. In the mordanting of cotton, an additional operation—viz., that of *ageing*—is frequently employed, especially for piece goods. The prime object of ageing is to cause the mordant (*e.g.*, basic sulphate or acetate of alumina), which the material retains by capillary attraction, to decompose evenly on and in the fibres. Sometimes, as is for instance the case with ferrous acetate, a simultaneous oxidation takes place. Ageing * is effected by suspending the material in ageing rooms, in which the temperature and degree of moisture of the atmosphere are kept as constant as possible in order to allow of a gradual and even deposition of the mordant on the fibre. The operation usually requires from one to three days.

In the *application* of the *direct dyes* the methods employed call for no special comment. The material is simply immersed in the cold, warm, or boiling dye solution, and moved there continuously or intermittently until the required shade is obtained. After dyeing, in many cases, an after-treatment is necessary either for the purpose of developing the colour, rendering it brighter or more permanent, or giving a particular feel or handle to the material. Thus, in the dyeing of Alkali blues on wool or silk, it is necessary, in order to fully develop the colour, to pass the material after dyeing through a hot bath of dilute sulphuric acid. Cotton material is frequently treated, after dyeing, with an emulsion of oil in soap in order, on the one hand, to give the material a better feel, and, on the other hand, to brighten the colour. The soap or oil emulsion is not washed out, and the material is dried with it in. The oil thus remains in the material and enhances the brilliancy of the colour, just as a varnish improves the appearance of the grain of a wood, or as water brightens the colours in a stone or pebble. Silk is frequently passed, after dyeing, through dilute tartaric, acetic, or sulphuric acid in order to give it the peculiar feel known as "scroop." Again, many of the direct cotton colours are rendered much faster to light by treating the dyed material for a few minutes in a boiling dilute solution of copper sulphate. The process is largely used, especially in the case of the blues, blacks, browns, greys, &c.

In the application of the *mordant dyes*, three distinct methods are employed That most generally adopted, which is known as the *mordanting and dyeing method*, is to dye the material which has been previously mordanted with the dyestuff, which may either be in solution (*e.g.*, logwood) or in a state of suspension (*e.g.*, Alizarin). The method termed in wool dyeing, *stuffing and saddening*, consists in first boiling the material with the colouring matter, as is, for

* The term ageing is also applied to the process of developing certain colours on the fibre. Of these, by far the most important is Aniline black, for the development of which the so-called rapid ager is largely employed (see *Aniline Black*).

instance, the case in the production of the old dyewood browns, with camwood, fustic, and logwood, and subsequently developing in the mordant solution (*e.g.*, chrome or copperas). This method is not so frequently employed at present in wool dyeing as formerly. With the so-called *Acid chrome colours*, such as Diamond black, the Erio chrome colours, &c., the mordant (bichromate) is added to the dye-bath after the latter has become exhausted. In cotton dyeing, chiefly in piece dyeing, this method of treatment is still much employed in the production of browns, drabs, and so-called "mode colours," but more especially in those shades in which catechu is employed as a constituent. A third, and last, method of employing the mordant dyes is the so-called single-bath process ("one dip" dyes). In both the preceding methods the insoluble colour-lake is produced on or in the fibre, but in the single-bath process the lake to be fixed on the fibre is rendered soluble in the dye-bath, and is taken up by the fibre like a direct dye, as is, for instance, the case in dyeing Cochineal scarlet or Flavine yellow on wool.

In order to obtain certain effects in dyeing, it is sometimes found advantageous to employ two dyestuffs of a totally different character, and to apply them two separate baths are required. Thus, wool to be dyed in the indigo vat is frequently previously dyed or *bottomed* with barwood. If the colouring matter is used after dyeing in the vat, as is the case in the use of Methyl violet on cotton, the operation is known as *topping*. The most extensive application of this process is in the topping of direct colours on cotton in a fresh bath with basic colours.

If the dyed material still containing the hot dye-liquor is allowed to lie in heaps, it is often noticed that the colour is thereby considerably deepened. Whether this is due to a process of oxidation, or to what one might term an after-dyeing, is not certain. Advantage is sometimes taken of this in "smothering" the goods after dyeing, as is, for instance, frequently done with direct blacks produced with logwood and copper on cotton.

Theory of Dyeing.—Towards the end of the eighteenth century, the interesting phenomena observed in dyeing had already attracted the attention of scientists, and numerous theories have since been brought forward from time to time with the object of explaining these phenomena. The majority of the theories advanced assume that dyeing is either due to a mechanical absorption of the particles of the colouring matter by the substance of the fibre (mechanical theory), or to a chemical combination of the colouring matter with the substance of, or some substance contained in, the fibre (chemical theory).

Hellot and Le Pileur d'Apligny in the eighteenth century were the first advocates of a strictly mechanical theory of dyeing. They assumed that all fibres are porous; that the pores of one fibre are of a different size to the pores of another fibre of different origin; and that the number of pores is greater in some cases than in others. Thus, wool was supposed to have the pores of greatest diameter, and in a given space the largest number of these, and silk those of least diameter. The pores are expanded by heat and certain chemical agents in such a way as to admit the particles of colouring matter, and then, being closed by cooling or astringents, were able to retain them securely. To explain why dyes would not enter into combination with all fibres equally, the theory of different-sized pores was invented, and then different sizes were attributed to the particles of colouring matters. They, of course, allowed (as do other advocates of a mechanical theory) the influence of mordants as forming insoluble lakes with the colouring matters.

Walter Crum,* another staunch supporter of the mechanical theory, maintained that, in order to be able to resist washing, the colour must be enclosed by the fibre as by a bag or fine network; the colouring matters must be in the

* *Journ. Chem. Soc.*, 16, i., p. 404.

cells or pores of the tissue. He considers that there can be no chemical combination with the fibre, for, to use his own words, "if we only consider that chemical attraction necessarily involves combination, atom to atom, and, consequently, disorganisation of all vegetable structure; that cotton wool may be dyed without injury to its fibre, and that the fibre remains entire, when by chemical means its colour has again been removed, we shall find that the union of cotton with its colouring matter must be accounted for otherwise than by chemical affinity." Crum admits a power of attraction on the part of the cotton fibre, and a capability of its withdrawing chemical or colouring substances from their solutions. But in this force he only recognises that same action which enables charcoal to absorb gases, and remove colouring matters, and some salts and metallic oxides from solutions.

More recently, the mechanical theory has found another prominent adherent in Müller-Jacobs, who, in his series of articles on "Membranous Diffusion in Dyeing" in the *Textile Colorist* for 1885,* bases all the phenomena as observed in dyeing on exosmosis and endosmosis.

His conception of the dyeing process is essentially the same as that of Hellot and Le Pileur d'Apligny—viz., that the textile fibres contain cavities into which the colouring matters enter by diffusion. The reason why vegetable membranes are less easily dyed than those of animal origin is found in the much greater permeability of the vegetable membranes. Their power of absorbing dyestuff is, however, much increased if the interstices of the fibre (*e.g.*, cotton) be much reduced, as by the mercerising process. According to this author, the *rôle* of mordants is, not only to combine with the dyestuffs to form insoluble precipitates, but also to reduce the permeability of the fibre. As a proof of this, he states that Alizarin red requires for the full development of the colour fifteen times as much of aluminium hydrate as would be necessary for the formation of a normal aluminium alizarate.

G. v. Georgievics† is also entirely opposed to the idea of any chemical change taking place in the fixation of the dyestuff by the fibre. In reference to Knecht's work on the decomposition of the basic dyes by the wool fibre (see below), he maintains that, not only wool, but also such indifferent substances as unglazed porcelain and glass beads‡ will decompose Magenta, hydrochloric acid being left in solution, and a coloured red substance remaining on the object.§ The dyeing of wool with Magenta is explained by this author by the assumption that in the first instance a dissociation of the Magenta takes place into hydrochloric acid, and a coloured ammonium base of rosaniline,|| which latter is mechanically taken up by the fibre by a process of "adsorption."

* See also *Journ. Soc. Dyers and Col.*, 1885 and 1886.

† *Journ. Soc. Dyers and Col.*, 1895, pp. 79 and 121.

‡ Magenta solution, evaporated down slowly in presence of crushed Jena glass in a dust-free atmosphere, does not show this phenomenon. Regarding the behaviour of coal-tar colours towards starch, silicic acid, and silicates, see also W. Suida, *Journ. Soc. Dyers and Col.*, 1904, p. 277.

§ It is not stated whether the hydrochloric acid is free or combined.

|| H. Weil (*Journ. Soc. Dyers and Col.*, 1897, p. 38) disputes the existence of a coloured ammonium base of rosaniline, and asserts that the supposed coloured base of v. Georgievics owes its colour to the presence of unchanged Magenta in the precipitate. v. Baeyer regards the existence of a coloured ammonium base in the sense referred to by v. Georgievics as improbable. On the other hand, A. Hantsch (*Journ. Soc. Dyers and Col.*, 1900, p. 129) comes to the conclusion that three different rosaniline bases are capable of existing —viz., (1) the true-colour ammonium base, which is red; (2) the pseudo-ammonium base (carbinol base), which is colourless; and (3) the anhydride base, which is again coloured. Of these bases, however, the pseudo-ammonium or carbinol base is the only stable one, the other two passing over into this modification by a mere standing in aqueous solution. If v. Georgievics's theory were correct, wool dyed with Magenta would soon become decolorised if kept out of contact with the air to prevent the formation in the fibre of carbonate of rosaniline.

In regard to acid dyes, this author concludes that, because the animal fibres take up a larger proportion of the acid colours in presence of an excess of sulphuric acid, the chemical theory of dyeing is utterly fallacious. He argues that, since sulphuric acid is a much stronger acid than indigodisulphonic acid (?), an excess of the former should not be favourable in silk dyeing to the formation of a salt-like combination between the fibroïne and the colouring matter.

Experiments were also conducted by v. Georgievics, with the object of ascertaining whether, in dyeing silk with indigo extract, Henry's law of distribution (as stated by van t'Hoff and Nernst) was fulfilled—*i.e.*, whether the amounts of colour taken up by the fibre (C_s), and left in solution (C_w), gave constant values for the expression $\frac{C_s}{C_w}$. This was not found to be the case. He maintains, however, that in dilute solution most processes of dyeing took place according to the equation—

$$\frac{\sqrt[x]{C_s}}{C_w} = \text{constant},$$

in which x denotes the affinity of the colouring matter to the fibre.

L. Hwass* and G. Spohn† endeavour to explain the dyeing process by the action of molecular forces of a physical or mechanical character. The latter proved by means of microscopical examinations that cotton-dyed chrome yellow contains mechanically deposited crystals of lead chromate. Even the dyeing of Alizarin red on cotton he regards as a deposition of the same alizarin-alumina lake as can be obtained without the presence of the fibre.

J. Walker and J. R. Appleyard,‡ from the results of an exact investigation which they carried out on the amount of Picric acid taken up by silk from aqueous solutions under different conditions (without additions to the dye-bath), came to the conclusion that a real equilibrium is attained, which is independent of the original distribution of the materials. On the other hand, diphenylamine, when "dyed" in a solution of Picric acid, remains unchanged up to a certain temperature, but the moment this temperature is reached combination takes place with the formation of a definite coloured picrate.

Most other authors distinguish strictly between the dyeing of animal and of vegetable fibres. In the first case the process is generally admitted to be of a chemical character, but in the case of the vegetable fibres a mechanical theory is generally admitted.

Thus C. O. Weber§ defines the dyeing of cotton with the benzidine dyes as an aqueous solution of a dye of very small coefficient of diffusion formed inside the cellular cavities of the cotton fibre by means of a dye-bath possessing a high osmotic pressure. The fastness of those dyes as regards "bleeding" off the fibre is proportionate to the inertia of diffusion of those dyes, and inversely proportionate to the magnitude of their diffusion coefficient. In support of this theory this author points out (p. 125, *l.c.*) that dinitrocellulose dyes with the benzidine dyes exactly like ordinary cotton. But the same dinitrocellulose dissolved in acetone and produced as a fibre does not dye. The explanation is that the former contains cellular cavities capable of retaining water, while in the latter the presence of cavities is excluded. The coefficients of diffusion of the coal-tar colours to which reference is made do not, however, appear to have been determined.

Gnehm and Rötheli ‖ showed that when cotton is dyed with direct colours it takes up the dyestuffs in an unchanged condition. Thus cotton dyed with

* *Färber Ztg.*, 1890-91, pp. 221 and 243.
† *Dingler's Polyt. Journ.*, 1893, p. 210.
‡ *Journ. Chem. Soc.*, 1896, p. 1334.
§ *Journ. Soc. Chem. Ind.*, 1894, p. 120.
‖ *Journ. Soc. Dyers and Col.*, 1898, pp. 190 and 215.

the barium salts of Benzopurpurin 4 B and of Benzoazurin 3 G showed on analysis the presence of barium in amounts corresponding to the dyestuffs absorbed. From their investigation these authors come to the following conclusions:—The dyeing of different fibres is not a uniform process, and the dyeing of vegetable fibres does not depend upon the same processes (or only partially), as in the case of animal fibres. Even with these latter different phenomena take place, mechanical effects accompanying chemical reactions.

In a later publication on the subject, Gnehm* somewhat modifies his views with regard to the dyeing of cotton with the direct colours, pointing out that the free colour acids may also act as dyestuffs.

According to F. Krafft,† dyeing consists, in the great majority of cases, of the separation of colloid (adhesive and resistant) salts on or in the fibre. In support of this theory he points out that the molecular weights (determined by the boiling-point method) of rosaniline hydrochloride, Methyl violet, and Methylene blue are apparently much higher in aqueous solution than in alcoholic. Tannic acid is a colloid, as is, likewise, tannate of antimony. The compounds of the phenol-like dyestuffs (such as Alizarin) with mordants (like aluminium and ferric hydrates) are also colloid in character. Like Weber and Gnehm, he asserts that the direct cotton colours are fixed on cotton in an unchanged condition, the dyed material giving the same reactions as the free dyestuff. This is explained by assuming that in aqueous solution, by reason of their relatively high molecular weights, these dyestuffs are more or less sparingly soluble colloid substances, Benzopurpurin showing in aqueous solution an approximate molecular weight of 3,000 by the boiling-point method. Additional evidence of its colloid character is furnished by the fact that when its aqueous solution is placed in a parchment bag, and this in distilled water, no diffusion of the dyestuff takes place, even after several weeks' immersion, whereas dyestuffs like Magenta and Methylene blue began to diffuse after one or two hours.

In the dyeing of wool and silk a separation in the fibre of colloid or membranous salts also takes place (according to the same author), in the formation of which, however, the fibre itself takes a part. This is due, in the case of wool, to the presence of lanuginic acid, a substance which is capable of combining with both acids and bases.

The colloid theory originally put forward by Krafft has of recent years found more adherents, especially in Biltz, Dreaper, and Linder and Picton.

Biltz ‡ experimented with colloid solutions of certain metals and inorganic salts as dyestuffs, and appears to regard the colloidal character as an essential property of a dyestuff. He regards the dyeing process as a solution of a colloid in a colloid. In a further communication,§ he points out that there is no essential difference between the dyeing properties of coloured inorganic colloid substances and organic dyestuffs. Similar results to those observed on cotton were obtained by "dyeing" aluminium hydrate with Benzopurpurin. Experiments carried out with dialysed solutions of the Immedial colours on cotton and on inorganic hydrogels (aluminium, stannic, and ferric hydrates) showed an analogous behaviour.

This author admits, however, that the colours obtained with the colloid metals are very loose to washing, while their fastness to rubbing would appear to leave much room for improvement. His method of dyeing the Immedial colours is not in accordance with the practical mode of procedure, and it is doubtful whether true dyeing, in the ordinarily accepted sense, has taken

* *Journ. Soc. Dyers and Col.*, 1902, p. 142.
† *Ibid.*, 1899, p. 211.
‡ *Ibid.*, 1904, p. 145.
§ *Ibid.*, 1905, p. 276.

place in any of these cases except that of Benzopurpurin 4 B, and, in this one, a careful revision of the experiment failed to corroborate the published results.

Linder and Picton,* experimenting with a colloid solution of ferric hydroxide (hydroxychloride), found that this was coagulated by Soluble blue or Alkali blue, but not by Methyl violet. The solution is also coagulated by ammonium sulphate, but, beyond the point at which the coagulum separates, the excess of ammonium sulphate remains in solution. With Aniline blue this is not the case; the coagulum, after separating, continues to take up the dye with avidity, and the coagulum is "dyed." On the other hand, it was found that a colloid solution of arsenious sulphide was coagulated by Methyl violet, hydrochloric acid remaining in the solution, while Aniline blue had no coagulating effect. Magenta and Hofmann's violet behaved in a similar way. In these cases also the coagulum was capable of taking four or five times the amount of colour of that which was necessary to form the coagulate. The action is considered to be of an electrical character, taking place between two of the positively charged basic hydrosols, Methyl violet and ferric hydroxide, on the one hand, and the two negatively charged acidic hydrosols, Aniline blue and arsenious sulphide, on the other. Any two oppositely charged hydrosols in dilute aqueous solution combine to form a pseudo solution, the compound aggregates of which possess electric properties which depend on the relative proportions of the constituents present—*e.g.*, excess of Methyl violet (+) with Aniline blue (−) is electro-positive. Any two oppositely charged hydrosols in strong aqueous solution are mutual coagulants—*e.g.*, Methyl violet (+) aggregates, and, finally, coagulates Aniline blue (−). Furthermore, the hydrogels which separate when ferric hydroxide and arsenious sulphide are coagulated by metallic salts still retain the same selective affinity for the dyes which will coagulate them. The authors regard this fact as evidence that the granular aggregates in these hydrogels still retain some charge, and look upon these simple processes of substantive dyeing as taking place in two stages—(1) the coagulation stage, in which simple ionic interchange takes place between the "fibre substance" (colloid) and the dye, resulting in the separation of insoluble dye derivatives retaining a feeble charge; (2) the colour absorption stage, in which coagula produced in the first stage attract and retain the oppositely charged particles of the dye substance.

Dreaper,† from the results of a series of experiments with Primuline on silk, came to the conclusion that dyeing depends primarily on a diffusion process, obeying a modified form of the general laws of osmosis, supplemented in some cases, if not all, by a chemical or series of chemical reactions between the fibre and the dye.

The same author ‡ has since modified his views, and now attributes the bulk of the phenomena to physical causes. According to him, it would seem that dyeing may take place as a direct result of the following phenomena:—

1. A solution state of the dye within certain limits of aggregation, as determined by the laws of size.

2. A fibre state corresponding to this state of aggregation and of a permeable nature.

3. Localisation of the dye within the fibre area, due to surface concentration phenomena.

4. Localisation of salts, acids, &c. (assistants), within the fibre area.

5. Indirect entrance of dye aggregates by molecular migration with subsequent reformation of aggregates within the fibre area, according to the laws of size.

* *Journ. Soc. Dyers and Col.*, 1906, p. 210.
† *Ibid.*, 1904, p. 111.
‡ *Ibid.*, 1905, pp. 118 and 136

6. De-solution, due to concentration effects on secondary attraction between the fibre substance and the dyes.

7. Primary or chemical action may play some part at this stage, and may even, in rare instances, take the place of de-solution phenomena.

8. Dissociation effects in the case of basic dyes which may lead to the production of very basic salts in a high state of aggregation within the fibre area.

O. N. Witt* regards the fibres as solid solvents, which in dyeing extract the colouring matter from the aqueous solution of the dye-bath; just as, for instance, ether will extract or dissolve out resorcin from its aqueous solution if shaken with it. The degree to which the dye-bath will be exhausted will depend entirely upon the relative solubility of the colouring matter in the dye-bath (water), and in the substance of the fibre. In his interesting treatise on the subject, Witt gives numerous examples in illustration of the correctness of his theory. The main support of the theory is the result of the following experiment:—If a skein of white silk is heated in a solution of Magenta, the colour is abstracted from the solution and the silk is dyed red. If this red silk is now put into alcohol and warmed, the colour passes from the silk into the alcohol, in which Witt claims that it is more soluble than in the substance of the fibre. But if the solution be diluted with water, the colour returns to the silk.

Sisley† sought to confirm Witt's theory by substituting a neutral solvent, such as amyl alcohol, for silk as a means of extracting the coloured rosaniline from a colourless aqueous solution. Knecht‡ showed, however, that if the amyl alcohol is free from organic acids and the carbonic acid of the air be excluded no colouration of the amyl alcohol takes place.

The chemical theory may be said to have more adherents than the mechanical theory. In the eighteenth century already, Bergman and Macquer strongly opposed Hellot and Le Pileur d'Apligny. Subsequently the chemical theory was further supported, notably by Persoz, Berthollet, Chevreul, Kuhlmann, O'Neill, and others. In the second volume of his work on Calico Printing, Persoz considers cotton and other fibres to have an actual influence of a chemical nature upon salts. Thus aluminium acetate is much more completely decomposed upon cotton cloth than when it is spread over a similar surface of glass, mica, or platinum, which are chemically inactive.

In their composition and their general behaviour towards chemical agents it has been seen that the animal fibres differ entirely from those of vegetable origin. While the latter are regarded as hydroxyl compounds, and only possess slightly acid and basic properties, the animal fibres possess pronounced acid and basic properties; to this fact no doubt is due their power of combining with a much larger range of colouring matters than is the case with the vegetable fibre.

The chemical theory is mainly supported by the following considerations:—

1. The textile fibres possess either acid or acid and basic properties. This is shown in the first place by their well-known property of absorbing acids, alkalies, and certain salts from aqueous solution, and retaining them tenaciously.§ A further proof is furnished by the thermo-chemical researches of L. Vignon.‖

2. All dyestuffs possess either acid or basic properties or represent salts of bases or acids. It is, therefore, not unreasonable to suppose that in the

* *Journ. Soc. Dyers and Col.*, 1890, p. 173.

† *Ibid.*, 1900, p. 112. ‡ *Ibid.*, 1900, p. 123.

§ See Mills and Takamine, *Journ. Chem. Soc.*, March, 1883; also Fürstenhagen and Appleyard, *Journ. Soc. Dyers and Col.*, 1888, p. 124.

‖ *Journ. Soc. Dyers and Col.*, 1890, pp. 86 and 120.

process of dyeing, salt-like combinations insoluble in water (colour lakes)* should be formed between dyestuff and fibre (or a constituent of the latter).

When wool or silk is dyed with hydrochlorides of the basic colours, it seems evident that such a change takes place,† the whole of the hydrochloric acid remaining in solution, whilst the colour base (in itself colourless) is taken up by or combines with the fibre (or a constituent of the fibre).‡

Furthermore, Jacquemin pointed out in 1876 that when wool is boiled in a colourless solution of rosaniline base it is dyed red,§ and the same is found to be the case with silk. Since the dyeing even takes place in presence of a small amount of caustic alkali, it is evident that the production of a colour in the wool must be due to salt formation of some kind. The contention of v. Georgievics that a coloured rosaniline base is absorbed by the fibre cannot hold good for reasons given in the footnote on p. 9. Another most interesting and conclusive piece of evidence that salt formation takes place in the dyeing of wool is given by Nietzki.‖ The ethyl ether of tetrabromphenolphthaleïn is yellow, but its salts are blue. If silk is dyed in the slightly acidulated solution, it is not dyed yellow, as one would expect if simple mechanical absorption took place, but is dyed blue, in consequence of salt formation.

Reychler¶ records the results of some interesting experiments which strengthen the chemical theory as far as the dyeing of wool with basic colours is concerned. He determined the electrical conductivity of the exhausted dye-baths in which wool (which had been previously boiled several times with water alone) had been dyed with Magenta, Chrysoidine, and Vesuvine. The following is a summary of his conclusions:—In dyeing, wool is brought into contact with a very dilute and perfectly dissociated colouring matter possessing a salt-like character.** The reactions which take place indicate that the two constituents of the salt act independently of each other. The colour base reacts with the wool, being fixed by some acid group of the keratine, probably with elimination of water. The hydrochloric acid, on the other hand, behaves exactly as a free acid of the same concentration would. It saturates the bases which the action of water alone liberates from the fibre, and extracts from the wool besides an amount of basic substances sufficient to completely neutralise the solution. The conductivity of solutions in which wool has been dyed with Magenta, and in which wool has been boiled in hydrochloric acid equivalent in amount to that present in the Magenta, is the same in each case (about 60×10^{-6}).

Vignon†† has attempted to define the dyeing processes as dissociation phenomena. According to his views, a system of three substances—viz., the fibre, the dyestuff, and the solvent—takes part in every dyeing process and

* Binz and Rung (*Journ. Soc. Dyers and Col.*, 1902, p. 11), and Binz and Schroeter (*ibid.*, 1904, p. 106, and 1907, p. 16), while admitting the probability of salt formation in many cases, carry the matter a point further, and state that in dyeing wool with substantive colours it is probable that the fixation of the colour is due to a condensation of the substance of the fibre with the desmotropic quinonoid nucleus of the dyestuff.

† Knecht and Appleyard, *Journ. Soc. Dyers and Col.*, 1888, p. 72.

‡ Liechti (*private communication*) observed a similar phenomenon on boiling a solution of egg albumen with the hydrochloride of a basic dye; the albumen combined with the dyestuff, while the whole of the hydrochloric acid remained in solution. See also M. Haidenhain, *Arch. f. d. ges. Physiologie*, vol. xc., p. 115.

§ According to James Sharp (*Journ. Soc. Dyers and Col.*, 1885, p. 210) such a solution was largely used by the Yorkshire dyers for damasks five to eight years before the matter was brought forward by Jacquemin.

‖ *Chemie der organischen Farbstoffe*, 3rd Ed., p. 4.

¶ *Bull. Soc. Chim. de Paris*, 1897, p. 449.

** Miolati, *Ber.*, xxvi., p. 1788; Knecht, *Journ. Soc. Dyers and Col.*, 1893, p. 158, and 1897, p. 59.

†† *Bull. Soc. Ind. de Mulhouse*, 1893, p. 407.

between them an equilibrium is established, which is determined by the chemical forces and the dissociation conditions. From this it seems apparent that the law of multiple proportions is not applicable to dyeing processes. Most dyeing processes are, according to this author, of a chemical character, and can be explained from this point of view, especially if dissociation is taken into account.

In a subsequent publication * the same author gives the results of measurements of the molecular conductivities of some acid and basic dyes, which show that the ionisation is considerably increased by dilution, and especially by a rise in temperature. This explains, according to the author, the reason why dyestuffs are more completely exhausted from a dilute than from a concentrated bath.

That hydrolytic dissociation plays some part in dyeing was shown by some experiments recorded by Knecht.† If a drop of an aqueous solution of Magenta is placed on filter paper, it rapidly spreads and forms a red blot. Very soon, however, the blot or disc is surrounded by a colourless halo of liquid which attains its maximum size in the course of some minutes. The colourless halo was found to consist not of pure water but of a solution of hydrochloric acid. By using more and more dilute solutions of Magenta, the size of the colourless halo increased. Crystal violet and Methylene blue behaved similarly, but Methyl green, which does not dye wool well, only began to show a halo on being strongly diluted. A solution of caramel, which though more or less intensely coloured has no dyeing properties, gave no halo whatever. It was further shown that if increasing amounts of hydrochloric acid were added to the solutions of basic dyes, the halo gradually diminished in size, and when the amount of acid was sufficient to prevent the formation of a halo, the solution had lost its property of dyeing wool. Alcoholic solutions of these basic dyes showed no halo, but were also incapable of dyeing wool. With acid dyes, such as Picric acid, Naphthol yellow and Orange II., a very small halo is formed even in very great dilution, but by the addition of hydrochloric acid to their solutions, the halo rapidly gains in size up to a certain point, with increasing amounts of acid and the dyeing power of the solutions is thus augmented.

Lanuginic and sericinic acids, both of which are soluble albuminoids (albumoses), and which are produced by the hydrolysis of wool and silk respectively, show the remarkable property of precipitating both basic and acid colouring matters from their aqueous solutions.‡ It has not been proved that these bodies actually exist as such in the substance of the fibre. It is possible, however, that they may be formed in the fibre during the process of dyeing by the slight hydrolysing effect of the boiling water or dilute acid, and combine in the nascent state with the colouring matter which is in the bath. Reychler (*l.c.*) showed that when wool is boiled with water, a small quantity of an albuminous substance passes into solution, which is capable of precipitating the basic dyes. Gardner § also isolated this substance, and gave to it the name "wool gelatine." Knecht || also drew attention to the property which wool gelatine possesses of precipitating the basic dyes, having overlooked the statement in Reychler's paper, where the property is only incidentally mentioned in a footnote.

The result of the following experiment affords further evidence of chemical action in dyeing:—Wool dyed with Night blue was extracted in a Soxhlet with alcohol, and the extract evaporated to a small bulk. This was warmed with barium hydrate solution to decompose the lake, and then filtered from the

* *Bull. Soc. Ind. de Mulhouse*, 1907, p. 82.
† *Journ. Soc. Dyers and Col.*, 1893, p. 158, and 1898, p. 59.
‡ Knecht and Appleyard. *Journ. Soc. Dyers and Col.*, 1889, p. 72.
§ *Journ. Soc. Dyers and Col.*, 1898, p. 167. || *Ibid.*, 1902, p. 102.

insoluble Night blue base. The filtrate was boiled, and carbonic acid passed through the boiling solution for the removal of the barium. The solution filtered from the barium carbonate and evaporated down to a small bulk was found to possess the property of precipitating the basic colours. When evaporated to dryness it left a mass resembling dried glue, which, when heated, gave off a smell of burning horn. Silk, treated in the same way, gave similar results, and similar results were also obtained by substituting Crystal violet for Night blue.

From these considerations it seems evident that the dyeing of wool and silk with the basic colours is a chemical process. The dyestuff does not go into the fibre in an unchanged condition (as is assumed by most supporters of the chemical theory), its basic constituent only being taken up and combining with a portion of the fibre, forming a highly coloured and insoluble compound (lake) which is probably held in the fibre in a state of solid solution.* This condition would also account for the transparency of the dyed fibre.

With regard to the dyeing of the animal fibres with acid dyes, different conditions prevail. These dyestuffs are (with one or two exceptions) the alkali salts of sulphonic acids of the aromatic series. In the neutral condition, they exhibit (with few exceptions) but little affinity for the animal fibres,† and the use of acid as an assistant in dyeing is necessary. In the majority of cases sulphuric acid is used, either alone or along with Glaubersalt, for this purpose. In dyeing with acid colours, it has been commonly supposed that the only function of the acid in the dye-bath is to decompose the alkali salt of the sulphonic acid, and thus render the latter capable of being taken up by the fibre, either by chemical or mechanical action. This decomposition of the salts of the sulphonic acid has, however, been based *a priori* upon a too liberal theoretical speculation. The sulphonic acids are, as a matter of fact, very powerful acids—so powerful, indeed, that they are, in many cases, capable of decomposing salts of sulphuric and hydrochloric acids. Thus, when indigo is warmed with strong sulphuric acid, so as to produce the disulphonic acid, and the solution thus obtained is poured into a concentrated solution of common salt, the colouring matter is completely precipitated, not in the form of free disulphonic acid, but as its sodium salt.‡ An equivalent amount of free hydrochloric acid must, therefore, remain in solution. In this case the formation of the precipitate takes place in presence of a large excess of salt, and the question of solubility no doubt plays an important part. But if dilute solutions of sulphuric acid and indigotindisulphonate of soda are brought together, there is no reason to suppose that double decomposition should not take place in accordance with the scheme—

$$C_{16}H_8N_2O_2(SO_3Na)_2 + H_2SO_4 \rightarrow C_{16}H_8N_2O_2(SO_3H)_2 + Na_2SO_4,$$

until a certain definite equilibrium is established. Up to the present, no experiments have been recorded which might throw more light on this important subject.§ This is, however, not astonishing considering the difficulties in the way of experimental work in this direction. For, although it should be theoretically possible to arrive at a definite conclusion by a quantitive determination of the alkali metal left in solution, or in the ash

* Knecht, *Journ. Soc. Dyers and Col.*, 1889, p. 77.

† v. Georgievics mentions some notable exceptions to this rule, among them Orange G. Quantitative experiments with this dyestuff, in which the amount of colour left in the bath was estimated by means of $TiCl_3$, showed, however, that the amount of colour taken up is very small, being less than one-seventh of that taken up in dyeing under normal conditions.

‡ Regarding the behaviour of some other free sulphonic acids of dyestuffs, see Sisley, *Bull. Soc. Chim. d. Paris*, *l.c.*

§ Gnehm (*Journ. Soc. Dyers and Col.*, 1898, p. 191) has shown that when wool is dyed with the benzidine salt of Naphthol yellows the organic base remains in solution.

of the dyed wool, there were practical considerations which rendered this an extremely tedious and uncertain process. By employing the pure crystallised magnesium salt of Crystal scarlet in dyeing it was, however, found possible to arrive at a definite solution of the problem. Wool was dyed with 10 per cent. of this compound and an amount of sulphuric acid in excess of that required to liberate the free sulphonic acid.* The magnesium was then estimated in the bath, from which the colour had been completely exhausted. In a blank experiment, carried out with wool and sulphuric acid only, the amount of magnesium extracted from the fibre was estimated. When this was deducted from the total amount found in the first experiment, it was evident that the whole of the magnesium contained in the dyestuff had been left in solution, and that the Crystal scarlet had gone into the fibre in the form of the free colour acid. The magnesium salt of Crystal scarlet is not very soluble in water, and readily crystallises from comparatively dilute solutions. If, now, the dyestuff and sulphuric acid are boiled together in the same proportion as was used in the dyeing experiment, it was found that the bulk of the magnesium salt separated out unchanged on cooling. It is, therefore, evident that in the dyeing process the colour acid was withdrawn gradually and continuously, so that at the end of the operation the chemical change was complete.

The function of the acid in the dye-bath is, however, not by any means restricted to its decomposing the salts of the colour acids, although it appears probable that in some cases the substance (or substances) of the fibre is in itself sufficient to accomplish this.

It has been shown by Hallitt† that the free colour acids of acid dyes do not dye wool any better than their alkali (Na) salts. This observation has since been corroborated by others. On the other hand, it was shown by Knecht‡ that if wool is first boiled with 5 to 10 per cent. sulphuric acid, and is then extracted by repeated boiling with distilled water until it no longer yields a trace of free acid to the water, it dyes fuller shades in the neutral bath of acid colours than are obtained in dyeing in the ordinary way with acid in the bath. § Now, if wool is boiled in dilute sulphuric acid, the extract does not yield a precipitate with Crystal scarlet, but if the acid is taken of such a strength as to disintegrate the fibre, a substance is found in the solution which yields a copious and intensely coloured lake with this dyestuff. The inference from these observations is that the chief function of the acid in the dyeing of animal fibres with acid colours is to produce in the fibre a lake-yielding substance during the process of dyeing. Here, as in the case of the basic colours, we may consider the colour lake to be held in a state of solid solution by the substance of the fibre. || What the nature of the lakes thus formed is, we prefer for the present to leave an open question, although definite opinions have been expressed on the subject by different authorities. Thus, Gnehm¶ draws attention to the fact that the compounds of the basic colours with organic acids of high molecular weight (*e.g.*, stearic acid) are highly coloured and insoluble, while acid colours, like Naphthol yellow, yield

* Knecht, *Journ. Soc. Dyers and Col.*, 1907.

† "The Theory of the Acid Dye-bath," *Journ. Soc. Dyers and Col.*, 1899, p. 30.

‡ *Journ. Soc. Dyers and Col.*, 1888, p. 107.

§ Regarding the modifying action of other reagents on the dyeing properties of wool, see Gelmo and Suida, *Journ. Soc. Dyers and Col.*, 1905, p. 277; 1906, p. 164; and also the patents of Meister, Lucius, and Bruning (*ibid.*, 1901, p. 266), and the B.A.S.F. (*ibid.*, 1903, p. 71).

|| It is noteworthy that the lakes formed from lanuginic acid and acid dyes melt on being heated under water to temperatures above about 90° C., and solidify again on cooling to form aggregates which are so intensely coloured as to sometimes appear black.

¶ *Journ. Soc. Dyers and Col.*, 1898, p. 190.

insoluble salts with bases of high molecular weight (*e.g.*, benzidine). In a sense these salts are analogous to lakes, inasmuch as they are formed from soluble dyestuffs, are intensely coloured, and insoluble. Nietzki's experiment with the ethyl ether of tetrabromphenolphthaleïn (see p. 14) is also strong evidence of salt formation. On the other hand, Prudhomme* has shown that indifferent liquids, which do not mix with water, can be "dyed" with basic colours (by agitating them with their aqueous solutions) if they contain an acid, like salicylic acid, in solution; while if they contain a basic substance, such as acetanilide, in solution they can be "dyed" with acid colours.

An argument frequently advanced as antagonistic to any chemical conception of the process of dyeing is that there is no evidence of chemical action taking place during the process, such as alteration in temperature, a more or less complete change in the properties of the reacting substances, and, above all, the absence of any regularity in the quantities of the reacting substances. Commenting on this subject as far back as 1860, Chas. O'Neill † pointed out that Crum's objection, that if there were chemical combination there should be disorganisation of the fibrous structure, is ruled out of order by choosing gun-cotton as an example. This substance, though deeply and permanently altered in its chemical properties, would pass in the hands of most persons as ordinary cotton. O'Neill further remarks that in dyeing only a very small portion of the fibre is in actual combination, and this contention is borne out by more modern investigations with colouring matters which were then unknown.

That, however, in the dyeing of wool, the laws which govern chemical combination are to some extent obeyed, is shown by the fact that acid colouring matters of analogous composition, or belonging to homologous series, are taken up in dyeing (under exactly similar conditions and using a large percentage in each case) in the proportion of their molecular weights.‡ The same applies to the homologous basic dyestuffs pararosaniline hydrochloride and Crystal violet. The observation made during the course of these experiments that, in dyeing with the acid colours, the amount of water in the dye-bath had no material influence on the amount of colour taken up is *prima facie* evidence that, in these cases at least, there can be no question of "solid solution" taking place, in the sense attributed to the expression by Witt. Furthermore, it would be difficult to explain, except by the assumption of chemical action, how it is that the free colour acids, which are generally extremely soluble in water, should be held by wool in such a manner that they will withstand the action of boiling water.

Of all the theories advanced with the object of explaining the dyeing of animal fibres with substantive colours, it would appear then that that based upon chemical interaction between the fibre (or certain constituents of the fibre) and the dyestuff best explains the phenomena. The existence of pores in the fibres and their assumed influence on the dyeing process has been greatly exaggerated. When viewed under the microscope in section, it is seen that, in dyed fibres, the colour permeates more or less uniformly the whole mass of the fibre, although it would appear that, in the case of an animal growth like wool, some portions show more affinity for the dyestuff than others. That pores can have no influence, or at least no material influence, on the dyeing process is proved by the fact that artificial fibres made from cellulose or gelatine, in which the presence of pores is excluded, behave in dyeing like the natural ones.

The purely colloid theory advanced by Biltz is based upon too slender evidence to allow of its general application. Besides, it fails to explain the

* *Rev. gen. d. Mat. Col.*, 1900, p. 184.
† *Chemistry of Calico Printing, Bleaching, and Dyeing.*
‡ Knecht, *Journ. Soc. Dyers and Col.*, 1889, p. 74; 1904, p. 242.

opposite effects which the addition of an electrolyte, like sodium sulphate, exerts in the dyeing of direct colours on cotton and acid colours on wool. The arguments in favour of this theory also start with a false premiss—viz., that all dyestuffs are colloids—which is unfounded. That the fibres themselves are of a colloidal character there appears to be no doubt, and their compounds with the dyestuffs will probably also possess this character. Although numerous investigations have been recorded within recent years, by which our knowledge of the colloids generally has been considerably extended, nothing has been done in those of the class which constitute, or are derived from, the textile fibres. The conclusions drawn by analogy with other remote phenomena in colloid precipitation are not of much intrinsic value in explaining dyeing processes.

With regard to the dyeing of cotton and other vegetable fibres,* practically all who have expressed themselves on the question are of opinion that the process is of a purely mechanical nature, as has been pointed out above. Nearly all the investigations which have been carried out in this respect refer to the dyeing of cotton with direct colours, and, from the imperfect manner in which these dyestuffs exhaust the bath in dyeing and their well-known property of bleeding, there seems to be strong evidence of purely mechanical action or solid solution. This is borne out by an extensive series of quantitative determinations conducted by one of the authors on carefully purified cotton yarn with chemically pure dyestuffs. The results show that the distribution of the dye between fibre and solute is in all cases strictly in accordance with Henry's law,† so that the solid-solution theory of Witt applies in these cases.

H. Erdmann ‡ has attempted to explain the dyeing of cotton on the assumption that cotton cellulose possesses a quinonoid structure, by virtue of which it shows some affinity for the benzidine derivatives. This explanation has, however, not met with universal approval.

While not venturing to express any definite opinion for the present, we will restrict ourselves to a statement of the following facts, which, while not definitely proving anything, tend to show that a chemical theory, as far as the dyeing of vegetable fibres is concerned, is not *a priori* out of the question.

Cellulose (see *Cotton*) is not by any means such an inert substance as it is usually supposed to be. It readily combines with acids to form definite compounds of different types, and is also capable of combining with the alkalies and other metallic hydrates as well as with ammonia. The compounds thus obtained are fairly definite in character, and have been well studied.

For the basic colours, cotton which is free from oxycellulose shows no affinity. But, if the acidity of the cellulose molecule is increased by the action of oxidising agents (formation of oxycellulose) the fibre shows a marked affinity for the basic colours. Nitrated cellulose will also take up basic colours, and if the same nitrated product be suitably denitrated, the affinity of the fibre for basic colours has disappeared. Acetylated and benzoylated cotton behave similarly. Thus, if cotton be boiled for a brief period with acetic anhydride, it is found to have become imbued with considerable affinity for basic colours. A short treatment in boiling dilute caustic soda suffices to destroy this property.

On the other hand, nitrated or acetylated cotton is found to have lost its

* Appleyard (*Journ. Soc. Dyers and Col.*, 1902, p. 102) mentions that, in the dyeing of jute with the basic colours, he finds that the same quantitative changes take place as in the dyeing of wool.

† The results obtained by v. Georgievics with Benzopurpurin, in which he asserts that the distribution takes place according to the formula $\frac{\sqrt{\text{C fibre}}}{\text{C bath}}$ = constant, are quite misleading, and this is probably also the case with the other direct colours which he experimented with.

‡ *Chem. Ind.*, 1896, i.

property of dyeing in the direct cotton colours, but this property is restored by denitration or saponification.

Furthermore, Vignon * has stated that, by introducing the amido group into the composition of the cotton cellulose (*e.g.*, by heating with calcium chloride ammonia), the fibre acquires an affinity for the acid colours.

Although it has not hitherto been possible to obtain a soluble derivative or decomposition product of cellulose which will precipitate the direct colours from their aqueous solutions, a derivative of the kind which will precipitate the basic colours can be obtained from tetranitrocellulose by dissolving in cold caustic soda and precipitating with hydrochloric acid. The precipitate after washing and drying constitutes an amorphous powder of a light cream colour, and is evidently an organic nitrate or contains organic nitrates. The substance is not readily soluble in water, but the aqueous solution yields with the basic colours intensely coloured lakes.

The *mordanting* of wool and silk appears to be analogous to the dyeing of these fibres, and to depend upon their acid and basic properties. Thus, wool boiled with a solution of aluminium sulphate fixes both the acid and the basic constituent of the salt; but, being possessed of more pronounced acid than basic properties, it absorbs the basic constituent more energetically than the acid one, and some free acid is left in the solution. By subsequent treatment with boiling water, more acid is extracted, and the alumina becomes more firmly combined with the substance of the fibre. It is noteworthy that only such salts which contain the acid and basic constituents in a comparatively loose state of combination are absorbed by the wool fibre. Thus, whereas the sulphates of aluminium, iron, chromium, and copper are readily taken up from the boiling solution by the wool fibre, sodium sulphate or sodium chloride are not taken up at all. Chromic acid, on the other hand, is readily taken up by wool, and, like the acetates of the heavy metals, is precipitated from its aqueous solution by lanuginic acid.

* *Journ. Soc. Dyers and Col.*, 1893, p. 44.

PART II.

CHEMICAL TECHNOLOGY OF THE TEXTILE FIBRES.

A KNOWLEDGE of the chemical and physical properties of the textile fibres, and of their behaviour towards the various substances which they are likely to come in contact with, either during the process of manufacture or afterwards, as well as their behaviour under varying conditions of moisture and temperature, is of the greatest importance both in dyeing and finishing. The two most important things which the dyer has to deal with are, in the first place, the material to be dyed; and, secondly, the materials or substances used in producing the desired colours and effects. Unfortunately, the exact study of the former subject (the textile fibres), from a chemical and physical point of view, has been somewhat neglected, and there are at present still many points on which more extensive and more exact information would be desirable. Chemists have hitherto usually turned their attention to more straightforward, and perhaps more remunerative, work; but, at present, increased signs of activity have shown themselves in this important field of research; and it is to be hoped that this will be rewarded by results valuable, not only from a theoretical but also from a practical point of view. Although it is generally admitted that a sound knowledge of the technology of the dyes, mordants, &c., renders a vast assistance to the dyer, this must be increased two or threefold when it is combined with a thorough knowledge of the technology of the textile fibres, or at least with as complete a knowledge as our present scientific status will allow of, and the student will, therefore, see the necessity of devoting his close attention to this subject.

The textile fibres are usually divided according to their origin, and the great differences in their chemical and physical properties, into two great classes *—viz., *the vegetable fibres* and *the animal fibres*, which may again be subdivided into several divisions, of which the most important member is usually taken as the typical representative.

Of the vegetable fibres cotton is the most important, and it is this fibre on which we possess the most detailed information. Then follow linen, hemp, jute, Chinagrass, and a host of other vegetable textile fibres, some of which have indeed met with a small demand in the market; while by far the greater number are merely museum specimens, and are likely to remain such. Although one sometimes comes across one of these fibres which, from the results of practical tests and experiments carried out on the small scale, promises good results as a textile fibre, the hold which cotton and linen have

* In some works the *mineral fibres* form a third class. These comprise asbestos, glass wool, slag wool, &c., but as these fibres are of very minor importance in the textile industries (except as packing for steam joints, and for covering boilers and steam pipes), and are never submitted to any processes of dyeing or bleaching, they will not be considered in this work.

on the market almost invariably renders successful competition a practical impossibility. Of other vegetable substances which the dyer frequently has to deal with may be briefly mentioned: straw (for hats), vegetable ivory (for buttons), and wood. Paper, for the manufacture of which various vegetable substances are used, may vary considerably in its chemical properties according to the material from which it has been made.

The animal textile fibres include wool, hair, and the different kinds of silk. To the same class belong such substances as feathers, horn, bone, ivory, and leather. These substances are nitrogenous, and differ entirely from those of vegetable origin, not only in their chemical, but also in their physical properties; and, consequently, require a different treatment in bleaching, dyeing, and finishing. They will not withstand such high temperatures as those of vegetable origin; while at the same time they are more capable of resisting the action of mineral acids, but are much less stable towards alkalies than the latter. In addition to these properties, they have the power of combining directly with a much larger number of colouring matters, and possess the property of assimilating directly metallic bases from certain salt solutions.

THE VEGETABLE FIBRES.

COTTON (Germ., *Baumwolle;* Fr., *Coton.*)

The working of cotton into fabrics originated, so far as we know, in India, the first allusions to cotton clothing extant being in Herodotus (B.C. 445). Some hundred years later we are told that the Hindoos wore "a sort of linen made from a stuff which grew upon trees." Pliny speaks of the Egyptians wearing cotton goods. The Chinese also used them; in fact, they claim to have manufactured cotton goods as far back as 2,300 years B.C. Prior to the discovery of America the inhabitants of Mexico, Brazil, and Peru appear to have been well acquainted with the methods of spinning, weaving, and dyeing of cotton, and beautiful examples of their skill in this respect are, from time to time, brought to light by the excavation of tombs. Spain was the first European country to manufacture cotton, and in the thirteenth century her products reached a high degree of excellence. The Dutch afterwards became very famous in the handicraft, and it is undoubtedly to the latter nation that we owe the success of the early manufacture of cotton in Great Britain. Probably the first mention of the trade in Lancashire and district is contained in Lewis Roberts' *Treasury of Traffic*, published in 1641, in which, speaking of Manchester, the author says:—"Neither doth their industry rest here, for they buy cotton-wool in London that comes first from Cyprus and Smyrna, and at home worke the same and perfect it into fustians, velveteens, dimities, and other such stuffes, and then returne it to London where the same is vended and sold, and not seldom sent into forrain parts, who have means at far easier terms to provide themselves of the said first materials."

Raw cotton, as it comes into the market, consists of the hairy material which covers the seeds of various species of the cotton plant (*Gossypium*), which belongs to the natural order of the Malvaceæ or mallow-worts. The fibres are attached to the seeds, which latter are enclosed in a 3 to 5 valved capsule. When ripe, this bursts and exhibits a ball of snowy white, or slightly yellowish fibre. The cotton is picked as soon as possible after ripening, and comes into the market after having been separated from the seeds by an

operation termed "ginning." The seeds, which were formerly not considered of any value, are now used in the manufacture of cotton-seed oil (of which they contain 20 to 25 per cent.), large quantities of which are used for soap making and other purposes. The crude oil as well as the cake are coloured yellow to brownish-yellow. The *colouring matter* to which this is due is contained in the fresh seed in colourless globules fairly regularly distributed throughout the mass of the starchy matter. It has been obtained in the form of well-defined yellow crystals, to which Marchlewski * has given the name gossypol, and to which he ascribes the formula $C_{18}H_{14}O_4$. The crystals melt at 188°. In strong sulphuric acid it dissolves with a characteristic crimson colour, and this solution if poured into water yields a yellow precipitate. In caustic alkalies gossypol readily dissolves to an intensely yellow coloured solution. Mordanted cotton can be dyed with it in various shades of yellow to brown. The residue of seeds, from which the oil has been expressed, is known as cotton-seed cake, and constitutes a valuable foodstuff for cattle. The complete separation of seed particles from the fibre is not always possible, and they are frequently visible in grey calico in the form of black specks or "motes." These may, under certain conditions, give up part of the oil or tannin which they contain to those portions of the cloth which are in the immediate vicinity, and thus give rise to unevenness in dyeing.

There are four primary species of the cotton plant, which appear to include all those which are usually cultivated for commercial purposes. These are:—

1. *Gossypium Barbadense.*—This is the most valuable, being the one which produces the long silky-haired Sea Island cotton. The *Gossypium hirsutum*, which is supposed to be a variety of *G. barbadense*, is the one from which the greater portion of the United States and the Egyptian (macco or Jumel) crops are raised.

2. *Gossypium Peruvianum* is indigenous to South America, and flourishes in Peru, Brazil, and the neighbouring countries. The flowers are yellow.

3. *Gossypium herbaceum* is a native of Asia, and is a small shrubby plant bearing a yellow flower. It produces the Madras, Surat, short-stapled Egyptian, and some qualities of American cotton.

4. *Gossypium arboreum* is also found in India and China, and is a fine tree-like plant, bearing a reddish flower, and yielding, under suitable conditions, a long silky cotton.

Practically considered, the best division is (according to Bowman) that of herbaceous, shrub and tree cotton. In one or other of these forms the plant is indigenous to the warm climates, but especially in India, Egypt, and America. The herbaceous cotton is the most valuable, and is that from which the large American crop is obtained. The shrub is about the size of an ordinary currant bush, and in the hottest climates becomes perennial.

Physical Properties.—Bowman defines the typical cotton fibre as a long tubular compound vegetable cell, from 1,200 to 1,500 times as long as it is broad. The outer sheath appears to be a continuous liber cell of pure cellulose; and the inner or thickening layers of the tube consist of secondary cellular deposits upon this epidermic layer, or are formed by a gradual thickening of that layer itself. The thin end of the fibre is closed; while the other—viz., that by which it was attached to the seeds, is irregularly torn. When viewed under the microscope, the cotton fibres present the appearance of ribbons, thicker as a rule at the edges than in the middle, and are frequently seen to be spirally twisted. This spiral shape of the fibre is due to the drying up of the sap originally contained in the ripe fibre. When seen in reflected light the fibres exhibit a lustrous surface. In transverse section the normal cotton

* *Journ. Chem. Soc.*, 1899, p. 84.

fibres present a great variety of shapes, but they are all more or less flattened, and in each is visible the small opening which runs from the base almost to the extreme end of the fibre. The special character of the fibre renders it suitable for the manufacture of very fine yarns; and also accounts for the elastic character of fabrics made from cotton as compared with linen fabrics, of which latter the fibres are stiff and straight.

In the perfectly ripe cotton the tubular form is distinctly seen in section, but the young unripe fibres show no indications of a tubular structure. Under the microscope they present the appearance of broad ribbon-like fibres, which are almost transparent and show irregular folds. Such fibres, which are technically known as *dead cotton*, are difficult to dye, and may sometimes be met with in indigo or alizarin-dyed calico in the form of white specks.*

The length and diameter of the cotton fibres vary considerably according to their origin, as will be seen from the following figures quoted by Evan Leigh:—

Description of Cotton.	Length of Staple in Inches.		Diameter of Fibre in Inches.	
	Min.	Max.	Min.	Max.
New Orleans,	0·88	1·16	0·000580	0 000970
Long Stapled (Sea Island),	1·41	1·80	0·000460	0·000820
Brazilian,	1·03	1·31	0·000620	0·000960
Egyptian,	1·30	1·52	0·000590	0·000720
Native Indian,	0·77	1·02	0·000649	0·001040

Expressed in millimetres, the mean length of the cotton fibre varies between 15 and 60, and the diameter from 0·010 to 0·040.

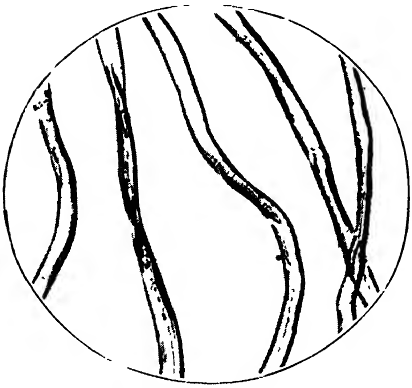
As a rule the longest fibres have the smallest diameter, and are finer and silkier in the staple; they can be spun to the finest counts, and command the highest price in the market. We obtain an idea of the minuteness of an individual cotton fibre when we remember that if all the fibres contained in a single pound of American cotton were placed end to end in a straight line they would reach 2,200 miles. The strength of the individual cotton fibres is also subject to considerable variations, as will be seen from the following figures, which represent the results of experiments carried out by Chas. O'Neill. He arranges them as follows:—

	Mean Breaking Strain in Grains.
Sea Island (Edisto),	83·9
Queensland,	147·6
Egyptian,	127·6
Maranham,	107·1
Bangueld,	100·6
Pernambuco,	140·2
New Orleans,	147·7
Upland,	104·5
Surat (Dhollerah),	141·9
,, (Comptah),	163·7

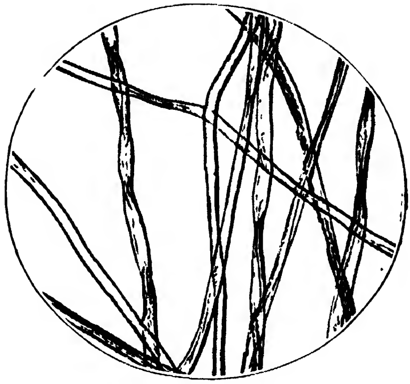
Speaking roughly, the fibre which carries the highest strain has the largest diameter, and, therefore, the largest sectional area to resist the breaking. The ripe fibres—that is, those in which the sectional area is greatest—are consequently able to resist a greater strain than the unripe fibres of one and the same quality. When subjected to tension, the walls have a tendency to collapse; and, when the flattening process has gone so far as to obliterate the whole of the central opening, the extreme outer structureless pellicle seems to suffer rupture first, while the inner parts of the tube-walls seem to extend

* According to A. Flatters (*The Cotton Plant*) dead cotton is more probably an over-developed fibre.

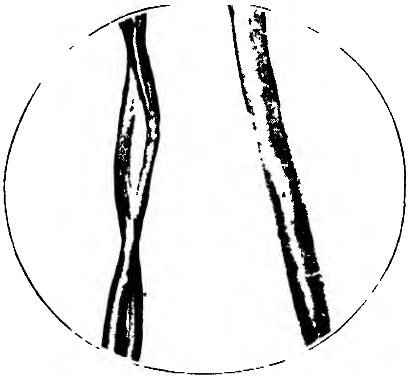
Plate I.



No. 1.—Indian cotton (Assam). × 75 diam.

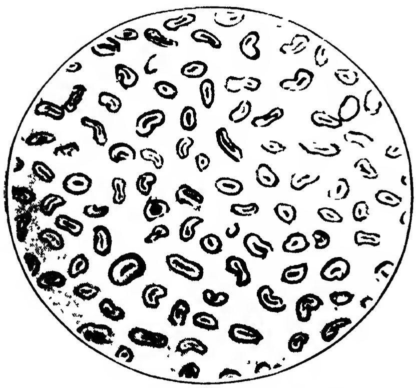


No. 2.—American cotton (Gallini). × 75 diam.

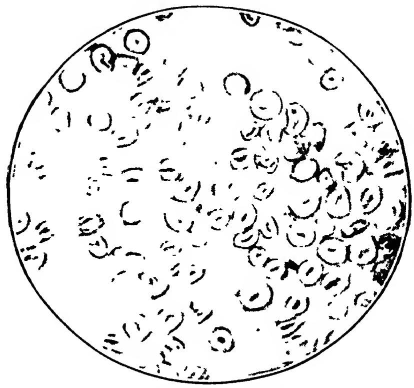


No. 3.—Sea Island cotton (Florida). × 160 diam.

No. 4.—Sea Island cotton mercerised under tension. × 160 diam.



No. 5.—Sea Island cotton (cross-section). × 160 diam.



No. 6.—Cross-section of Sea Island mercerised cotton under tension. × 160 diam.

[*To face p.* 24.

slightly, and then the whole completely severs. This severing is usually accompanied by a drawing-out of portions of the secondary deposits which remain, after the rupture is complete, in the form of fibrous masses, giving a very ragged edge to the fractured tube.

In the unbleached condition the cotton fibre is covered with a thin membrane or *cuticle*, the presence of which is best revealed by observing the action of Schweizer's reagent (see below) on it under the microscope. Under the influence of this reagent the fibre rapidly swells, causing the cuticle to burst in places, while, in others, it forms strictures round the greatly distended fibre. Mercerised and well-bleached cotton do not show this behaviour, since the cuticle is practically all destroyed by mercerising or bleaching.

It has frequently been stated that, when a wet cotton fabric freezes, it is tendered in consequence of the bursting of the fibres. Exact experiments carried out by C. F. S. Rothwell * show that, even when frozen several times over, no appreciable diminution of the strength of cotton fabrics takes place. Naturally, when a fabric is frozen stiff, it will break when folded or crumpled, but the same would take place if it were stiffened with a strong gum solution and dried.

Up to a certain degree, the action of *heat* is such as to influence only the physical properties of the cotton fibre. Heated to 100°, the fibre loses its natural hygroscopic moisture, or (as Bowman terms it) its water of hydration, which amounts under ordinary circumstances to from 6 to 8 per cent.† When exposed to the air again at the ordinary temperature the fibre rapidly regains weight until it has absorbed just as much moisture as it gave off. The rate of absorption varies, however (as might be expected), with the hygrometric condition of the air, being much slower in fine, dry weather than in foggy or wet weather. The maximum amount of hygroscopic moisture which the cotton fibre is capable of absorbing is, according to Wiesner, just under 30 per cent. The strength of cotton yarns and fabrics is very materially influenced by the amount of moisture present. Thus, cotton dried at 100° C. is much weaker than the same material containing the normal amount of moisture, while, in the wet state, it is stronger than in the ordinary condition. At 100° C. the moist cotton fibre becomes plastic, although not to the same extent as is the case with wool. The fibres may be made (under the influence of pressure) to assume at this temperature certain shapes, or may be made to lie in certain directions, retaining their position after cooling. On this property are based the various processes of hot-finishing (calendering, &c.).

According to L. Vignon, loose cotton possesses, in the air-dried condition, a specific gravity of 1·50.

Counts of Cotton Yarn.—The fineness of cotton yarn is expressed by so-called "counts," or numbers which indicate how many hanks of 840 yards each go to a pound. Thus by 60's cotton is meant a yarn of which 60 hanks of 840 yards each would be required to make a pound.

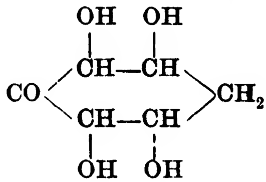
Chemical Composition and Properties.—Cotton, freed from the natural impurities, which it invariably contains in greater or smaller quantities, consists of almost pure cellulose, a substance which is universally distributed throughout the vegetable kingdom, and which forms (either as such or in some modified form) the so-called ligneous or woody fibres of plants. But whereas in the cotton fibre cellulose exists in an almost pure condition, it is generally accompanied in other plant fibres by a greater or less amount of incrustaceous matter which is usually difficult to remove. The impurities contained in raw cotton amount to about 5 per cent. by weight, and consist, essentially, of pectic acid, colouring matter, cotton wax, cotton oil, and albuminous matter. The

* *Journ. Soc. Dyers and Col.*, 1892, p. 153.

† The standard adopted by the Manchester Chamber of Commerce is 7·8 per cent.

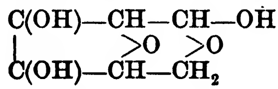
process of *bleaching* has for its object the removal of these substances, and will be referred to again under that heading.

The chemical analysis of cellulose shows that it consists of carbon, hydrogen, and oxygen, and that the simplest formula representing its composition is $C_6H_{10}O_5$. It belongs to a naturally occurring important class of substances, which are chemically known as carbohydrates, of which starch, dextrin, and the sugars may serve as familiar examples. These bodies may be looked upon as polyatomic alcohols, containing at the same time aldehyde or ketone groups. According to the investigations of Cross and Bevan, cellulose forms a penta-acetyl derivative, and might consequently be regarded as a pentatomic alcohol, $C_6H_5(OH)_5$. These authors, however, do not regard cellulose as a pentatomic alcohol. They consider that it contains only three hydroxyl and one aldehyde group, while the fifth oxygen atom is in combination with two carbon atoms, forming the group $=CH-O-CH=$. The penta-acetyl cellulose would appear to be formed by a more profound change, involving disintegration of the molecule. Under normal conditions, only four acetyl (or three acetyl and one benzoyl) groups can enter into chemical combination. In the double molecule, $C_{12}H_{20}O_{10}$, they regard eight of the ten oxygen atoms as being present as hydroxyl groups, while the other two are present either as ketone or aldehyde groups. Based upon these considerations, these authors (in collaboration with Beadle) suggest that cellulose consists of groups of the type—



which unite with each other by virtue of the CO and CH_2 groups to more complex molecules.*

A. G. Green,† who bases his conclusions to a large extent on the researches of Fenton, has suggested for cellulose the following formula—



by which it is represented as an intramolecular anhydride of glucose.

Pure cellulose is usually regarded as a somewhat inert substance; it is colourless, possesses neither taste nor smell, and is absolutely insoluble in water, alcohol, ether, and other ordinary solvents. Its specific gravity is about 1·5. When heated, it first parts with its water of hydration; and, if heated still further, it turns brown. The temperature at which cellulose begins to be permanently altered has been variously stated, and the figures differ enormously (from 130° to 270° C.). This is no doubt due to the time factor not having been taken into consideration. That decomposition takes place, even at 100°, is known to most chemists from the fact that filter papers left in a water oven for some considerable period are found to have acquired a yellow tinge, and to have become quite friable. C. O. Weber (private communication) placed the lowest temperature at which cotton suffered a permanent change at 80° C., and this he calls its "critical temperature."

Light also exerts a disintegrating action on the cotton fibre, which is best

* *Journ. Soc. Chem. Ind.*, 1893, p 498.

† *Journ. Soc. Dyers and Col.*, 1904, p. 117.

noticed in the tendering of muslin and lace curtains and window blinds. This tendering is probably due to the formation of oxycellulose. In this connection it is interesting to note that ship's sails dyed with cutch are said to last much longer than white ones.

If strongly heated in closed vessels cellulose is ultimately completely decomposed, yielding water, acetic acid, methyl alcohol, acetone, and other products similar to those obtained in the dry distillation of wood, and leaving behind a residue of charcoal. In the open air it burns freely without emitting any very strong smell, but smouldering cotton gives off the characteristic penetrating smell of acrolein.

Action of Water.—Under ordinary conditions water has no action on the cotton fibre, but, when heated under pressure to 150° with water, A. Scheurer finds that the fibre is sensibly attacked. Raw cotton subjected to this treatment for eight hours had decreased in strength from 18 to 17, bleached cotton from 27 to 20. When heated with water to 200° cotton turns brown, and is decomposed with the formation of carbonic acid, formic acid, pyrocatechin, glucose, &c. Prolonged steaming at 99° to 100° C. also has a tendering effect, which, after 420 hours, amounts to about 75 per cent.

Solvents for Cellulose.—When treated with an ammoniacal solution of copper hydrate,* the cotton fibre swells up considerably and slowly dissolves, forming a thick slimy solution, from which acids throw down a gelatinous precipitate. According to A. Flatters † the newest layer—*i.e.*, the portion of the fibre closest to the inner cell wall—is attacked, and dissolved first. According to the same authority mildew is found to exert a similar action, inasmuch as it first attacks the cellulose nearest to the inner cell wall. The cuticle and the endochrome are not dissolved. This, when washed and dried, forms an amorphous white powder possessing the same chemical composition and properties as the original purified fibre. It is, therefore, regarded as unchanged cellulose. Prudhomme,‡ however, maintains that oxycellulose is formed by the action of ammoniacal copper solution on cellulose. This author does not state, however, whether his Schweizer's reagent was freshly prepared or not. When kept for some time in contact with the air, the reagent takes up a considerable amount of oxygen and is known in this condition to oxidise many organic substances. Experiments which we have conducted in order to decide this question show that filter paper dissolved in freshly prepared Schweizer's reagent and then precipitated by hydrochloric acid yields a cellulose which only takes up a very small amount of Methylene blue, and this absorption is no doubt due to the small amount of oxycellulose already present in the filter paper (according to Nastukoff about 5 per cent.). By allowing the solution of the filter paper in Schweizer's reagent to stand for some time in contact with the air, it was found to yield a less copious precipitate on acidulating, and this gave, with Methylene blue, a much deeper shade than the one which was precipitated at once.

Cellulose also dissolves, according to Cross and Bevan,§ in a solution of zinc chloride (1 part) and hydrochloric acid (2 parts), showing a specific gravity of about 1·44. By pouring this solution into water, a precipitate of cellulose is obtained which contains 18 to 25 per cent. ZnO. A solution of cellulose in zinc chloride has been suggested by Manby for the production of a permanent filling in calico. This solution may also serve in place of albumen as a fixing agent for pigments in printing.‖

* This solution, which is generally known as Schweizer's reagent, may be prepared as follows:—To a cold solution of copper sulphate add ammonium chloride, then caustic soda in excess. Filter, wash, and dissolve in ammonia of 0·92 specific gravity.

† *The Cotton Plant.*

‡ *Journ. Soc. Dyers and Col.*, 1891, p. 148.

§ *Chem. News*, 1891, pp. 63, 66.

‖ English Patent No. 10,466, 1894.

An ammoniacal solution of nickel hydrate dissolves silk, but not cellulose.

Behaviour towards Acids.—Concentrated mineral acids usually exercise a very powerful and rapid action on the cotton fibre, but this may vary considerably according to the kind of acid, temperature, and duration of contact.

Concentrated sulphuric acid first causes the cotton fibre to swell up, forming a gelatinous mass; and, if this is rapidly diluted with water, a precipitate is obtained of a substance termed *amyloid* which is coloured blue by iodine solution. The formation of vegetable parchment is supposed to be due to the partial transformation of the vegetable fibres into this substance. A more probable explanation is that the fibres are superficially converted into cellulose sulphates,* which, on coming into contact with the water, decompose with regeneration of cellulose, which sticks the fibres together and fills up the interstices. Vegetable parchment is prepared by passing unsized paper into cold sulphuric acid at 140° Tw., allowing it to remain in the liquid for not less than five, and not more than twenty seconds, and then thoroughly washing out the acid in plenty of water. Paper treated in this manner is found to have decreased in volume, but to have increased in density, while, at the same time, its strength has increased three to four fold. The same treatment is said to impart to the cotton fibre an increased affinity for the basic coal-tar colours.

By the continued action of strong sulphuric acid cotton is completely dissolved and is converted into a gum-like substance, chemically known as dextrin, which possesses the same empirical composition—viz., $C_6H_{10}O_5$. If the solution is diluted and boiled for some time, the dextrin undergoes a further chemical change and is converted into glucose or grape-sugar, $C_6H_{12}O_6$. The close relationship which exists between these three carbohydrates is thus shown in a striking manner.

According to H. Koechlin, cotton steeped in the cold in *strong nitric acid* (83° Tw.) is converted into a dinitro-cellulose, the fabric being neither tendered nor rendered inflammable. Cotton thus treated had acquired an increased affinity for basic colours. Knecht† was not able to confirm this latter observation as far as the basic colours were concerned, but found, on the other hand, that the treated cotton had acquired an affinity for some acid colours. He further pointed out that when cotton is steeped for some minutes in nitric acid of 83° Tw., it assumes a gelatinous appearance, which disappears on washing with water. Calico thus treated was found to have shrunk considerably, and, while having gained in strength, had acquired a greatly increased affinity for the direct colours and the sulphide colours. It is noteworthy that, although the fabric thus treated does not shrink as much as when subjected to the action of caustic soda, its affinity for direct colours is twice as great as that of cotton mercerised in the ordinary way (in either case without tension). Twofold Egyptian cotton yarn, treated in a stretched condition with strong nitric acid, and washed until slackening ensues, acquires a silk-like lustre.

If the nitric acid is below 77° Tw., it does not show this peculiar action on cotton; on the contrary, the fibre is soon tendered by acid of lower concentration. In a subsequent communication,‡ Knecht showed that cotton which had been steeped in nitric acid of 83° Tw. could be dried in a vacuum over freshly burnt lime. The product thus obtained fumed strongly when exposed to moist air, and was found to contain 35·8 per cent. of loosely combined nitric acid, which would correspond approximately to the formula $C_6H_{10}O_5 \cdot HNO_3$. This unstable nitrate is decomposed instantly by water, to which it yields the whole of the loosely combined nitric acid.

It was further shown that if cotton be steeped for a prolonged period (four to

* See also Blondeau (*Berz. Jahresber.*, xxv., p. 282), Marchand (*ibid.*, xxvi., p. 615), and Fleischig (*Zeit. f. phys. Chem.*, vii., p. 528).

† *Journ. Soc. Dyers and Col.*, 1896, p. 89. ‡ *Ibid.*, 1904, p. 68.

six hours) in nitric acid of 84° Tw. it acquires a new and remarkable property—viz., an affinity for acid dyestuffs, such as Acid violet, Naphthol yellow, Crystal scarlet, &c. It is, therefore, in a sense *animalised* by this treatment.

Cotton treated with other volatile acids, such as anhydrous formic acid, glacial acetic acid, or concentrated hydrochloric acid, only retains 2 to 3 per cent. of acid after drying in a vacuum over burnt lime.

By strong hot nitric acid, cotton is entirely decomposed, a number of products being formed, including oxalic acid and an oxidised cellulose soluble in alkalies. A similar product is obtained by heating the loose nitrate alluded to above to 100°. Towards a mixture of strong nitric and sulphuric acids, the cotton fibre behaves in a different and somewhat peculiar manner. Its external appearance is not changed, but the cellulose becomes converted into a series of compounds, which are known as nitro-celluloses (more correctly cellulose nitrates), and which contain more or less nitrogen, according to the composition of the original mixture of acids. These bodies were first discovered in 1846 by Schœnbein. The most highly nitrated product hitherto described has the composition $C_{12}H_{14}(NO_2)_6O_{10}$, and is known as *pyroxylin* or *gun-cotton.* A less nitrated product (trinitro-cellulose), produced by the action of less concentrated acids on cellulose, is known as *soluble pyroxylin.* According to Lunge* a perfectly soluble pyroxylin, possessing the maximum degree of viscosity, is obtained by steeping carefully purified and dried cotton-wool for two hours at 40° C. in mixed acids containing—

42·36 per cent.,	H_2SO_4
41·10 ,,	HNO_3
15·50 ,,	H_2O

The mixture contained besides 1·04 per cent. N_2O_4. 73 parts of this mixture were used for 1 part cotton. The resulting product contained 12·42 per cent. nitrogen. It is soluble in a mixture of ether (2 parts) and alcohol (1 part); the thick solution thus obtained constitutes the so-called *collodion.* It is also soluble in acetone, amyl acetate, pyridine, and other organic solvents. When allowed to evaporate, these solutions leave behind a thin horny layer which is transparent and insoluble in water. On this account solutions of pyroxylin are used for coating book-cloths and "schreinered" cotton goods in order to render them water- or rain-proof.

Cotton treated with mixed acids shows an increased affinity for direct colours up to a certain degree of nitration, probably on account of the mercerising action which occurs. Beyond the condition of tetranitro-cellulose, however, this affinity begins to decrease, and with hexanitro-cellulose it is practically nil. On the other hand, highly-nitrated cellulose evinces a marked affinity for the basic colours. J. Schneider † has turned this property to account for dyeing two colours on cotton in one bath. If a portion of the cotton is mercerised (preferably with nitric acid), three colours result.

By *strong hydrochloric acid* cotton is disintegrated, especially when the material is dried with the acid in. It is thus reduced to a white powder. Gaseous hydrochloric acid reduces moist cotton to a gelatinous mass.

Dilute mineral acids have little or no action on cotton when cold. If cotton is exposed at the ordinary temperature for a few minutes to the action of sulphuric acid of from 104° to 125° Tw., and is then thoroughly washed, the strength of the fibre is (according to Mercer) not impaired; but it acquires an increased affinity for colouring matters. In the cold, sulphuric acid only changes the fibre when it is sufficiently concentrated to absorb more water with evolution of heat. According to C. Koechlin,‡ one may steep cotton in acid at 32° to 52° Tw., at 15° C., without injury, and it will only be at 69° Tw.

* *Zeitsch. f. angew. Chem.*, 1906, p. 2051.
† *Journ. Soc. Dyers and Col.*, 1907, p. 78. ‡ *Ibid.*, 1888, p. 103.

(3 parts acid to 8 parts water by volume) that the change is noticeable after the third hour. Cotton can withstand the action of sulphuric acid at 93° Tw., diluted by its own volume of water for one hour. In six hours the fibre is tendered and begins to absorb colour from a solution of Methylene blue; in forty-eight hours, the change and property of absorbing colour are complete. With sulphuric acid, containing 100 grms. per litre and heated to 80° C., no immediate change is effected; it takes five minutes for the change to begin, thirty minutes before it has made progress, and an hour for completion.

If cotton, saturated with dilute mineral acid,* be allowed to dry, the acid gradually becomes more and more concentrated on the fibre, and the latter is "tendered." The degree to which the tendering takes place will depend to a great extent on the temperature at which the drying is effected. Sharp drying at a high temperature has a much more destructive influence than slow drying. The same takes place when cotton impregnated with certain salts, such as the chlorides or nitrates of aluminium, iron, or chromium, is dried. A more or less complete dissociation of the salt takes place and the acid which is liberated tenders the cotton. Hence, it is obvious that all cotton goods or goods containing cotton should be well washed after being in contact with mineral acids, or with salts, which are liable to undergo dissociation, in order to avoid tendering in the drying operation.

Hydrocellulose.—When viewed under the microscope, cotton fibres which have been tendered by the action of acid do not appear to have undergone any physical change, but analysis shows that a chemical change has taken place which is evidenced by a slight increase in the percentage of hydrogen and oxygen. If the acid is taken strong enough, the cotton is completely disintegrated, and falls to a white powder. The product, to which the formula $C_{12}H_{22}O_{11}$ has been ascribed, has been termed *hydrocellulose.*† For its preparation, cotton is immersed for 12 hours at the ordinary temperature in sulphuric acid of 1·45 specific gravity, well washed, and dried at a moderate temperature. The chemical properties of hydrocellulose are similar to those of ordinary cellulose, from which it differs, however, in the following respects:—Heated beyond 40° in the air it oxidises and turns yellow, becoming blackened at 100°. It is soluble in boiling acetic anhydride, while cellulose is not. According to A. L. Stern,‡ cotton which has been disintegrated by acids and washed absolutely free from acid is not blackened at 100.° He considers that when cotton is disintegrated by acids this is due to certain portions being more easily attacked, and when these portions are converted into soluble products, the whole fibre falls to pieces. When cotton, which has been tendered by the action of acids (hydrocellulose), is mercerised, it gains considerably in strength, while if the tendering has been caused by an oxidising agent (oxycellulose), a diminution in strength is brought about by mercerising with caustic soda. Concentrated nitric acid appears to have the opposite effect. The following figures may serve to illustrate this remarkable behaviour:—

	Breaking strain.
Bleached cotton yarn,	557 grms.
,, ,, tendered by H_2SO_4,	366 ,,
Tendered yarn mercerised,	615 ,,

The tendered yarn placed in nitric acid of 83° Tw. was completely rotted.

Some of the same yarn was partially converted into oxycellulose by permanganate and then decolorised with bisulphite.

* It is interesting to note that in this respect benzene sulphonic acid behaves like a mineral acid.

† Girard, *Ber.*, 1881, p. 2834. ‡ *Journ. Soc. Dyers and Col.*, 1904, p. 121.

	Breaking strain.
Oxycellulose, ...	208 grms.
After immersion in HNO_3, ...	232 ,,

Placed in strong caustic soda the yarn was completely rotted.

The destructive action produced on cotton and other vegetable fibres by immersion in a dilute mineral acid, and then drying, is turned to practical account in the process of *carbonising* (*q.v.*).

Organic acids attack the cotton fibre to a much less extent than do the mineral acids; even when used boiling they do not, in moderate dilution, exert any action. When dried on the fibre and then steamed oxalic, tartaric, and citric acids may, however, produce tendering.* When a strong solution of oxalic acid thickened with gum is allowed to dry overnight on cotton fabric, no appreciable tendering takes place, but the printed portions are found to possess an increased affinity for basic and a decreased affinity for the direct dyes.†

Knecht‡ has shown that this remarkable phenomenon is due to the formation of formylcellulose, the oxalic acid decomposing on drying into carbonic and formic acids. A short treatment in boiling dilute caustic soda is sufficient to saponify the product, and the cotton acquires its normal properties again. Succinic acid does not show the reaction, but malonic acid and ethylmalonic acid, which, like oxalic acid, are decomposed by heat, show it in a marked degree.

Boiling acetic § and formic acids tender cotton when in the pure state, but in the dilute condition they do not appear to exert, under any conditions, a deleterious action on the fibre.

Heated with acetic anhydride, cotton is acetylated, yielding a monoacetylcellulose. By the action of acetic anhydride in presence of a dehydrating agent like concentrated sulphuric acid, triacetylcellulose || is formed, which is readily soluble in acetone. A formyl cellulose is obtained by the action of anhydrous formic acid on cellulose in presence of HCl. ¶

By acting on cellulose with a mixture of glacial acetic acid, acetic anhydride, and sulphuric acid, Cross, Bevan, and Briggs** have succeeded in preparing an acetosulphate of cellulose having the composition $(C_6H_7O_2)SO_4(C_2H_3O_2)_{10}$, which is soluble in alcohol.

Carbonising.—Woollen rags or loose wool are immersed for 2 to 12 hours in dilute sulphuric acid at from 2° to 8° Tw., the duration of the immersion depending upon the strength of the acid. After the excess of acid has been removed in hydro-extractors, the rags are carefully dried, first at a temperature of 30° to 45°, which is raised after two to three hours to 70° to 80°, at which temperature the vegetable fibre is carbonised. The material is now taken out, and the vegetable fibre, which crumbles to dust by friction, is mechanically removed. Bisulphate of soda has recently been suggested for carbonising in place of sulphuric acid, and is said to give very good results.

According to another method, which is sometimes employed for rags in the production of shoddy or mungo, the material is exposed to the action of dry hydrochloric acid gas in a revolving cylindrical cage which is contained in a cylindrical cased iron vessel heated by steam to about 100°.

Aluminium chloride is also used for carbonising. The action depends upon

* A. Scheurer, *Journ. Soc. Dyers and Col.*, 1893, p. 206; 1901, p. 156

† H.H.P., *The Dyer*, 1902, p. 91. ‡ *Journ. Soc. Dyers and Col.*, 1907.

§ Cross, Bevan, and Traquair (*Journ. Soc. Dyers and Col.*, 1905, p. 192) mention that cotton boiled with glacial acetic acid takes up 3·4 to 4·2 per cent.

|| See also C. O. Weber, *Journ. Soc. Dyers and Col.*, 1900, p. 7; and F. Marsden, *ibid.*, 1905, p. 102; also B.A.S.F., *ibid.*, 1905, p. 304.

¶ English Patent No. 2,511, 1907. ** *Journ. Soc. Dyers and Col.*, 1905, p. 133.

the fact that when an aqueous solution of aluminium chloride is evaporated to dryness, it is decomposed with the formation of hydrated alumina and free hydrochloric acid according to the equation :—

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl.$$

The liberated hydrochloric acid acts powerfully on the vegetable fibre which is destroyed, as in carbonising with sulphuric acid. The carbonising temperature for aluminium chloride is higher than for sulphuric acid. Magnesium chloride is also sometimes used for carbonising.

Behaviour towards Alkalies.—The action of alkalies on cellulose is very different from that of acids. Alkaline carbonates, and the milder alkalies, such as soap, borax, phosphate of soda, &c., have no action. Nor has ammonia, under ordinary circumstances, any effect on the cotton fibre. But if, according to L. Vignon,* cotton is heated under pressure with strong aqueous ammonia, or with the compound of ammonia and calcium chloride, to 200°, a nitrogenous product is obtained, which, although not differing from the original in external appearance, behaves towards the acid dyes like an animal fibre.

Dilute caustic alkalies or lime do not affect the fibre if, during the operation, air be excluded; but in presence of air, and at high temperatures, oxy-cellulose is readily formed, and the fibre is tendered. This circumstance is liable to give rise to faults in bleaching, and care must, therefore, be taken when boiling cotton goods with lime or alkali under pressure to exclude the air or to deprive it of its oxygen by means of some reducing agent. Even at the ordinary temperature cotton containing caustic soda undergoes a change of this kind, and the oxidation seems to be the more rapid the more concentrated the alkali.

Under the influence of concentrated caustic alkalies cotton is changed both physically and chemically. John Mercer, a Lancashire calico printer, first noticed, as long ago as 1844, the action of these reagents on the cotton fibre, and to him we are chiefly indebted for our knowledge of the subject.†

The discovery was really the outcome of an experiment carried out by Mercer in connection with the theory of solution, his object being to effect a partial separation of different hydrates of caustic soda by filtering its solution through cotton. For this purpose a filter was made, composed of six folds of strong bleached cotton cambric. A solution of caustic soda at 60° Tw. poured into the filter was found to pass through very slowly, and the density of the filtrate was only 53° Tw. At the same time the cloth used for filtering was found to have undergone an extraordinary change, having become semi-transparent, contracted both in length and breadth, and thickened or "fulled." When strong caustic soda was spotted in bleached cambric it was noticed that the central portion of each spot (about the size of a shilling) became translucent and contracted, and this was surrounded by a rim which was neither contracted nor translucent, and evidently contained but little caustic soda.

It was only some years later that Mercer found an opportunity of resuming his study of what he called "fulled cotton." He found that the alkali could be removed by washing in water, but that this required a much longer period than if the soda had merely been held mechanically. He concluded that a definite compound is formed with the alkali, which undergoes decomposition when brought into contact with water, or with the carbonic acid of the air. The compound formed by the alkali is represented by the formula $C_{12}H_{20}O_{10} . Na_2O$, and is decomposed by water into a hydrated cellulose,

* *Comptes rendus*, 1891, pp. 487 and 623.

† *The Life and Labours of John Mercer*, by E. A. Parnell. Longmans, Green & Co.

$C_{12}H_{20}O_{10} \cdot H_2O$, and caustic soda.* This latter formula nearly corresponds to the increase in weight (4·5 to 5·5 per cent.) which the treated cotton showed. At 100° this water of hydration is given off along with the hygroscopic moisture, but is taken up again when the fabric is exposed to the air.

Two other changes brought about by the action of the alkali by far outweighed in practical importance those already alluded to—viz., in the first place, increased tensile strength of the fabric, and, secondly, a considerable increase in its affinity for colouring matters—and these induced Mercer to take out a patent in 1850 for "Improvements in the preparation of cotton and other fabrics and fibrous materials," in the specification of which the process now generally known as *mercerising* is fully described.

Mercer obtained the best results by immersing the cotton cloth (which had been previously bleached, without being boiled, in weak alkaline liquors) in caustic soda at 45° to 50° Tw., but mentions that the change is sufficiently marked with ordinary bleached calico. The best results were obtained at about 60° F., for, although weaker liquor could be used by resorting to artificial cooling, the material turned out stiffer and harder. At a boiling temperature the effect could not be obtained. The linear contraction was found to be from one-fifth to one-fourth, and it was possible thus to contract fine cotton cloth containing 200 picks to the inch to 270 picks to the inch. Experiments made with regard to the increase in strength showed that a strip of calico which required before treatment a weight of 13 lbs. to break, required, after treatment, no less than 22 lbs. A bundle of threads which showed a breaking strain equal to 13 ozs. before treatment, required, after treatment, 19 ozs. to rupture them.

The increased affinity of mercerised cotton for the colouring matters is especially striking in the case of the direct cotton colours. This can be readily observed by dyeing together two fents of bleached calico (one mercerised, the other not) in Benzopurpurin for example. The colour produced on the mercerised pattern will be much fuller and deeper than on the ordinary calico. The increased depth of shade thus obtained is usually ascribed to the greater affinity of the mercerised cotton for the dyestuff. But if the dyeing is done in separate vessels with equal amounts of colouring matter, there is, after taking into account what dyestuff is left in solution in each case, a vast difference in favour of the mercerised cloth. No satisfactory explanation of this interesting fact has hitherto been brought forward. Mercerised cotton has also an increased affinity for tannin substances.

The caustic alkalies are not the only substances capable of bringing about the change in vegetable fibres known as mercerising. Thus sulphuric acid at 105° Tw. and chloride of zinc at 145° Tw. are mentioned in Mercer's original patent specification as exerting a similar action to that of caustic soda. According to the same authority, calcium chloride solution at 90° to 100° Tw. also has some effect at 290° F. Phosphoric acid and hot stannous chloride, containing three equivalents of water, are also mentioned by him as producing the effect. Nitric acid of 83° to 84° Tw. has a very similar action to caustic soda (see p. 28). According to Hübner and Pope,† a saturated solution of barium mercuric iodide also exerts an effect on cotton similar to that of caustic soda, but does not cause the loose fibre to untwist, as is the case with caustic soda and strong nitric acid.

* Shortly after Mercer's discovery became known, Gladstone extracted cotton, which had been treated with strong caustic potash, with alcohol, in order to remove excess of the reagent. The fibre thus extracted gave up to water the whole of the potash in combination, which was estimated and found to agree with the formula $(C_6H_{10}O_5)_2KOH$; in other words, it contained half as much alkali as Mercer's product.

† *Journ. Soc. Dyers and Col.*, 1903, p. 139.

The microscopical appearance of the cotton fibre before and after mercerising was studied by Walter Crum.* By examining cross-sections of these fibres he found that the action of the process was to cause the flattened fibre to assume the round solid form of ripe cotton, while at the same time the central opening is decreased in size. He considered the contraction of the mercerised fabric to be due to the twisting of the fibre under the influence of the alkali. The twisting of the fibre is also (according to Crum) much increased by mercerising, and there is a consequent shortening of it sufficient to account for the shrinking in length and breadth and the thickening of any woven fabric made to undergo the process. Diagonal lines are sometimes seen in these ripe mercerised fibres, giving the impression of a spiral structure; but they are evidently the creasing or corrugating effect of extreme twisting.

Experiments carried out by Chas. O'Neill with individual fibres of New Orleans cotton† showed that by the action of caustic soda of 50° Tw. the average shrinkage produced was 26 per cent., while the individual fibres gained somewhat under 12 per cent. in strength.

The fact that a French Company offered Mercer the sum of forty thousand pounds for the purchase of his patent rights, is sufficiently indicative of the importance which was at the time attached to his discovery. But, in spite of its advantages, the process was never, until recently, extensively used on the large scale. This appears to have been principally due to the surface contraction, which was then considered to be inevitable; and which, by increasing the price of the material, did not suit the merchants and manufacturers. About the year 1893 a process, originated by Mercer, of producing crimps on calico either by printing on thickened caustic soda or first printing on a gum resist and after drying passing through caustic soda, was re-introduced. Wherever the caustic soda comes into contact with the cotton the latter shrinks, and a crimp effect results.

Mercerising under Tension.—In 1889 H. A. Lowe ‡ took out a patent for mercerising cotton piece goods under tension, and this was supplemented by a further patent in 1900.§ In the specifications Lowe mentions that, in addition to obtaining the recognised advantages of mercerising (increased affinity for colouring matters, increased strength, &c.), a *permanent lustre* is imparted to cotton goods thus treated. Lowe's discovery did not receive at the time that recognition which it deserved, and, finding no encouragement, he allowed his patent rights to lapse. Messrs. Thomas and Prevost, who worked on similar lines with cotton yarn (Egyptian), apparently in ignorance of Lowe's previous work, also recognised that a permanent lustre could thus be obtained, and took out a patent for the process in Germany.‖ No sooner had this product been placed on the market than it aroused widespread interest, and at once created a demand. For some time mercerised yarn held the monopoly, but it was subsequently recognised that piece goods could also be treated (as described in Lowe's patents) with results not indeed so striking as those obtained on yarn, but, nevertheless, such as to produce a very material improvement in the appearance of the goods. The rapid increase in the demand for cotton goods mercerised under tension brought forth a flood of patented inventions for slight modifications in the method of treatment, but more especially in connection with machinery for the treatment of yarns and piece goods. Litigation with regard to the validity of Thomas and Prevost's patent resulted in its being annulled in all countries where an action was tried, on the grounds of prior publication in Lowe's patent specification, and the great majority of the subsidiary patents also fell or were allowed to lapse.

* *Journ. Chem. Soc.*, 1863, p. 407.
† *Textile Colourist*, June, 1876.
‡ English Patent No. 20,314, 1889.
§ English Patent No. 4,452, 1900.
‖ German Patent No. 85,564, 1895.

Mercerising under tension can be carried out in two ways. According to one, the cotton is stretched a little beyond its original length, and while in this condition * is immersed in, or saturated with, a strong solution of caustic soda (50° to 70° Tw.). Whilst still in the stretched condition the cotton is washed with water until the tension slackens. The goods are then removed from the machine, run through dilute sulphuric acid in order to neutralise the remaining caustic soda (which they would otherwise tenaciously withhold), and are then washed with water until free from acid. According to the second process, the goods are immersed first in caustic soda (50° to 70° Tw.) without tension, then stretched slightly beyond their original length, washed in this condition until slackening ensues, and then treated further as above. One or other of these principles is adopted in all mercerising processes carried out on a large scale (see Part IX.).

Cotton mercerised under tension exhibits varying degrees of lustre, according to the quality of the material and the structure of the yarn or cloth treated, but in all cases the lustre is permanent—*i.e.*, it is not effaced by washing, bleaching, dyeing, &c. The best lustre is always obtained on twofold or multifold yarns made from long-stapled Egyptian or Sea Island cotton, while yarn made from ordinary American cotton shows, as a rule, so little improvement in its appearance that the treatment is scarcely worth while. The same applies to single yarns, whatever kind of cotton they may be made of, and this fact is a great drawback to the manufacturer, since he is obliged, in order to obtain the desired effects, to employ the much more expensive doubled yarns where otherwise single yarns might serve his purpose.† It is thus evident that a successful process for obtaining a permanent lustre on single yarns would be of great industrial importance. In mercerising piece goods, the structure of the cloth has considerable influence on the result. Thus, a plain calico shows but little improvement, while face cloths, such as Italian linings or sateens, made from the same material may show, if well mercerised, a lustre almost equal to that of spun silk.

The *temperature* at which mercerising is effected is a question of considerable importance. This was known to Mercer, who recommended a temperature of 60° F. as the best for conducting the process. Any rise in the temperature during the impregnation with caustic soda ‡ above that of the atmosphere is deleterious to the result, while undue lowering of the temperature is apt to impart a harsh feel to the goods. At low temperatures, however, cotton can be mercerised with much less concentrated solutions of caustic soda than at the ordinary temperature. Thomas and Prevost patented the application of artificially-cooled caustic soda for this purpose, and maintained that, at 0° C., mercerising could be efficiently done with caustic soda of 15° to 18° Tw., a considerable saving in this material being thus effected. For a time, the low-temperature process aroused a considerable amount of interest, and some mercerisers were induced to put down refrigerating plant for the purpose; but, to-day, refrigeration is seldom employed beyond that which is necessary for preventing any undue rise in the temperature of the caustic soda.

The *strength* of the caustic soda used in continuous mercerising is generally

* In consequence of the enormous force exerted by the contracting fibres, it is necessary that the stretching appliances should be strongly made.

† In order to obtain single yarns of mercerised cotton various attempts have been made to mercerise the cotton before spinning, but the processes suggested have met with very limited success. In the process of Gros and Bourcart (English Patent No. 25,881, 1898), which has found some application on the large scale, a sufficient amount of twist is given to Egyptian sliver to enable it to resist the tension in mercerising. It is then wound into hanks, mercerised in the ordinary way, and then untwisted and spun as single yarn.

‡ Strong solutions of caustic soda when mixed with water produce a rise in temperature.

taken, in practice, at about 60° Tw.; for, although Mercer found that the process was complete with a lye of 45° Tw., he pointed out that, in passing through the bath, the cotton took out more caustic than that which corresponded to the liquor mechanically absorbed, and he even recommended that the caustic soda should be as strong as 65° Tw. at starting, but not weaker than 60° Tw.* For cotton pieces containing worsted, the caustic soda is sometimes taken of a strength of 80° Tw.

Mention is made in Mercer's and various other subsequent patent specifications of *reagents other than caustic soda* (caustic potash, sulphuric acid, zinc chloride, &c.) for mercerising cotton. From a practical point of view, however, these reagents have little or no interest, partly on account of their expense and partly because they are less effective than caustic soda. Some interest attaches, indeed, to nitric acid of 83° Tw., which was shown by Knecht not only to exercise an action similar to that of caustic soda in producing a lustre, but also to increase the affinity of the treated cotton for dyestuffs to double that of cotton mercerised with caustic soda. It is noteworthy that, if cotton is mercerised with caustic potash of 50° Tw., the contraction and increase in affinity for colouring matters are only about one-half of that of cotton mercerised with caustic soda of the same specific gravity.

The time required for mercerising was recognised by Mercer † as being of short duration—*i.e.*, a few minutes. Practical experience in the mercerising of pieces has since shown that the time in which the change is brought about is much less than a few minutes, and must, in fact, be measured by seconds. Some experiments were carried out by Knecht in this connection, by immersing bleached American cotton yarn (without tension) for periods varying from 5 to 120 seconds in caustic soda of 50° Tw., and then plunging the skeins at once into a large excess of cold dilute sulphuric acid. The skeins (the weights of which were ascertained before mercerising) were then dyed in 1 per cent. Benzopurpurin, and the colouring matter estimated on the fibre and left in solution by titration with titanous chloride.

Time.	Shrinkage.	Benzopurpurin taken up in Dyeing.
5 seconds.	15·7 per cent.	3·24 per cent.
10 ,,	17·4 ,,	3·62 ,,
20 ,,	25·0 ,,	3·80 ,,
40 ,,	25·0 ,,	3·89 ,,
60 ,,	25·0 ,,	3·91 ,,
180 ,,	27·4 ,,	4·10 ,,

From these figures it will be seen that, under the conditions, the greater part of the reaction had taken place during the first five seconds.

A permanent lustre can also be obtained on cotton by various processes *without tension*, but none of these have been successful on a practical scale. Thus, Meister, Lucius, and Brüning ‡ add for the purpose a strong solution of silicate of soda to the caustic soda. Bayer & Co.§ employ a mixture of 1 volume glycerine to 2 volumes caustic soda. The mercerising of loose cotton may also be effected by immersion in a hot solution of caustic soda at 80° Tw.,‖ but the process entails so much waste that it will not pay.

The mercerising of cotton fabrics on one side only by padding one side of

* E. A. Parnell, *Life and Labours of John Mercer*, p. 183. † *Loc. cit.*, p. 183.
‡ English Patent No. 10,784, 1897. § English Patent No. 27,050, 1897.
‖ See also Lowe, English Patent No. 17,397, 1897.

the goods with strong caustic soda by means of an engraved steel cylinder is the subject of a patent of Tagliani,* but the process only finds employment for printed goods.

Cotton mercerised under tension is modified in its properties like cotton mercerised without tension, but not to the same extent. From a practical point of view, the most important modification, next to the lustre, is the increase in depth of shade obtained in dyeing with a definite amount of colouring matter, compared with ordinary cotton dyed with the same percentage. A saving in dyestuff is thus experienced, amounting to some 25 to 30 per cent., and is especially noticeable in direct colours, sulphide colours, and colours like Aniline black and Paranitraniline red, which are produced on the fibre. The reason why mercerised cotton dyes so much darker than ordinary cotton with the same percentage of colour is not known. Possibly the removal of the cuticle in mercerising has something to do with it.

Although the *cause* of the increased lustre of cotton mercerised under tension has been the object of several extensive investigations,† in which different and, in some cases, antagonistic views are advanced, the explanation of the phenomenon is comparatively simple if we take into account the following facts:—When viewed under the microscope in *reflected* light the irregular surface of the cotton fibre is seen, at the points at which the light is reflected, to exhibit a strong lustre, and the same holds good for cotton which has been mercerised without tension. In yarn, however, but more especially in the piece, this lustre is not apparent, because the irregular reflecting surfaces of the fibres disperse the reflected light in every direction, and the impression produced in the eye is that of a dull or lustreless surface. The same holds good for cotton mercerised without tension. But if a large proportion of the fibres in a piece of calico are caused to lie in the same plane—*e.g.*, by passing the piece through a heated calender, a lustrous or glazed surface results. The effect is not permanent because the fibres have not been set by the treatment, and on being moistened with water resume their previous irregular positions, which results in the disappearance of the lustre. But if cotton yarn is mercerised under tension, it acquires, while saturated with the caustic soda, a gelatinous, and to some extent plastic, condition, so that the fibres, while becoming rounded and more translucent (and in this respect more like silk in structure), are drawn out and stretched, and become set in this position by the subsequent washing. We have consequently in the finished yarn a large proportion of stretched and straightened fibres, with a more or less round section lying parallel to each other, as in the case of spun silk, so that the inherent lustre of the fibre becomes visible to the naked eye.

It is frequently desirable to ascertain whether a cotton fabric has been mercerised or not, and although under ordinary conditions this would not seem to be a difficult problem, cases frequently arise, especially in Aniline blacks, in which the question can only be definitely decided by those who have gained considerable experience in such examinations. In case the fibre is not coloured it might be dyed along with some ordinary cotton of about the same quality in a dyestuff like Benzopurpurin, when an increased depth of shade would be a fairly sure indication that the sample had been mercerised. If the sample has been previously dyed it will be necessary, before carrying out the comparative dye-trial, to strip the colour, and this may be effected, as a rule, by treatment with acid or alkali, or with bleaching powder, or a reducing agent like titanous chloride, or hydrosulphite of soda. By carrying out

* English Patent No. 6,249, 1899.

† H. Lange, *Färber Ztg.*, 1895-96, p. 441, and 1898, pp. 197 and 234; E. Hanausek, *Dingl. Polyt. Journ.*, vol. cccvi. (1897), p. 19, and vol. cccvii. (1898), p. 180; Hübner and Pope, *Journ. Soc. Chem. Ind.*, 1904, p. 404.

quantitative dye-trials and estimating the relative amounts of colour which go on to the ordinary cotton, mercerised cotton, and the sample by titration with titanous chloride, it is even possible to ascertain roughly the strength of the caustic soda which has been used in mercerising.

Lange's test is also useful in detecting mercerised cotton, and is based upon the fact that when ordinary and mercerised cotton are steeped for a few minutes in a solution of iodine in potassium iodide and zinc chloride, they both turn blue, but on washing with water, the former is decolourised, while in the latter the blue colour persists. For preparing the reagent,* the following two solutions are prepared:—

SOLUTION No. 1.

5 pts. potassium iodide are dissolved in
16 ,, water, and
1 to 2 ,, iodine are added, and allowed to dissolve.

SOLUTION No. 2.

25 pts. zinc chloride are dissolved in
12 ,, water.

Solution No. 2 is stirred into solution No. 1 until iodine begins to separate. After allowing to settle, the clear dark brown solution is decanted from the sediment.

In carrying out the test, the sample to be examined should be immersed in the reagent *without* being wetted with water. Any samples which have been taken out of the reagent should at once be transferred to a beaker or dish containing distilled water and must not be exposed to the air. It is also of importance that the washing must not be conducted in running water.

In the case of Aniline blacks, the best means of examining the material is the microscope, and it is here that considerable experience is found to be necessary if a reliable result is to be arrived at.

Viscose.—If alkali cellulose—*i.e.*, cotton or some other form of cellulose which has been impregnated with caustic soda of 50° to 70° Tw. and then wrung or squeezed (without washing)—is exposed for some hours to the action of bisulphide of carbon vapour, a new cellulose compound is formed, which probably consists of a xanthate of cellulose, and to which the discoverers (Messrs. Cross, Bevan, and Beadle) have given the name viscose.† The product is soluble in water, with which it forms a viscous solution from which the viscose can be precipitated by the addition of common salt or of alcohol. Acids added to the aqueous solution precipitate the cellulose. In dyeing, viscose finds a limited application for book cloth, but is used sometimes as a filling for cotton goods, in calico printing, the manufacture of high-class wall papers, and in the production of viscose silk (see *Artificial Fibres*).

Behaviour towards Reducing and Oxidising Agents.—*Reducing agents* appear to have little or no action on cellulose, but energetic *oxidising agents* (like chromic acid, permanganate of potash, chlorine, chloride of lime, air in presence of alkalies, &c.) readily convert it into *oxycellulose*, a product first described by Witz.‡ The most striking property of oxycellulose is its affinity for the basic colouring matters, with which it can be dyed without the intervention of a mordant. The formation of this interesting product can be readily demonstrated by printing calico with a moderately concentrated thickened solution of chloride of lime, washing the material well after some time, and

* See also *Journ. Soc. Dyers and Col.*, 1896, p. 250.
† *Journ. Soc. Chem. Ind.*, 1893, p. 498; 1894, p. 900.
‡ *Bull. de Rouen*, 1882, p. 416; 1883, p. 169.

then dyeing in a cold solution of Methylene blue. The printed portions will be more or less of a dark blue, according to the duration of the action, while the untouched parts will only be tinted.

Oxycellulose may also be readily prepared by steeping cotton for some time in strong (12° Tw.) bleaching powder solution, or by heating the material in a solution of permanganate of potash until it has acquired a dark brown colour, and then decolourising with bisulphite. Steeping in a strong solution of bichromate, acidulated with 1 to 2 molecules of sulphuric acid, likewise produces oxycellulose. Its formation is invariably attended by a decrease in the tensile strength of the fibre, which, in the case of acid oxidising agents, becomes more marked by a subsequent alkaline treatment. Consequently the formation of oxycellulose finds no practical application; on the contrary, it is a thing to be avoided. Oxycellulose is not only formed by the specific oxidising agents alluded to, but in many other ways, and in some cases where one would hardly expect it. Thus, Witz showed that it is formed by the joint action of light and air on cotton fabrics, and this is especially noticeable in blinds and window curtains. Bleached calico exposed to direct sunlight for a period of two or three months during the summer is found to be appreciably tendered, and to have acquired an affinity for Methylene blue. Cotton containing caustic alkali or free lime may be tendered for the same reason when exposed to the air even at the ordinary temperature, but at high temperatures (as in the kier) the tendering is much more marked. Again, a partial conversion of the fibre into oxycellulose invariably takes place in bleaching with hypochlorites, and this becomes marked when the strength of the bleaching liquor exceeds 2° Tw. The formation of oxycellulose in Koechlin's method of discharging indigo in calico printing (printing on thickened chromate of potash, and then passing through a mixture of sulphuric and oxalic acids) is the most serious drawback to this process. According to Prudhomme,* oxycellulose is formed when cotton is boiled with peroxide of hydrogen and magnesia, while, under the same conditions, mercerised cotton is more strongly attacked. By the presence of metallic oxides the action is increased. This was corroborated by Knecht,† who showed that cotton mordanted with chromic oxide, when warmed with peroxide of hydrogen and ammonia to remove the chromium as chromate, became tendered through formation of oxycellulose; also by W. Thomson,‡ who, in examining some pieces which had been tendered in places in chemicking, found that the tendered portions contained copper. Metals themselves in presence of hypochlorous acid or hypochlorites may produce similar effects.§

With regard to the chemical composition of oxycellulose, little of a definite character can be stated here. Some suppose that there are different oxycelluloses, which are the result of employing different oxidising agents on cellulose. Others again maintain that cellulose cannot be completely converted into oxycellulose. Thus, Faber and Tollens ‖ assume that what we ordinarily call oxycellulose is a combination of a substance to which they give the name *celloxin*, of the formula $C_6H_{10}O_6$ (or $C_6H_8O_6$) with cellulose. The celloxin itself has not been isolated; it cannot be extracted by alkalies, as it is decomposed thereby into isosaccharic acid and dioxybutyric acid. Nastjukoff ¶ ascribes the formula $C_6H_{10}O_6$ to oxycellulose, according to which it would be cellulose with one atom of oxygen added to the molecule. Bumcke and Wolffenstein ** prepared oxycellulose by the prolonged action of a strong

* *Moniteur Scientif.*, 1891, p. 677
† *Journ. Soc. Dyers and Col.*, 1897, p. 109 ‡ *Ibid.*, p. 131.
§ A. D. White *Journ. Soc. Dyers and Col.*, 1903, p. 229.
‖ *Journ. Soc. Dyers and Col.*, 1899, p. 269.
¶ *Bull. de Mulhouse*, 1892, p. 493.
** *Journ. Soc. Dyers and Col.*, 1899, p. 269.

solution of hydrogen peroxide on cellulose. To the product thus obtained they gave the name *hydralcellulose.* This body is converted by caustic alkalies, in accordance with its aldehydic properties, into the corresponding alcohol (cellulose) and the acid (acid cellulose), which latter passes into solution, and can be thrown out again by the addition of an acid.

Oxycellulose forms a white amorphous powder, which evinces a strong affinity for basic colouring matters. According to L. Vignon,* it will take up as much as 0·6 per cent. Methylene blue, and 0·7 per cent. Safranine, whereas ordinary cellulose takes up only 0·2 per cent. Methylene blue (?). It also evinces a marked affinity for certain metallic hydrates. Thus it is capable of decomposing neutral solutions of aluminium and iron salts with the fixation of the corresponding hydrates, whose presence can be shown by dyeing in mordant colours like Alizarin. Stannous chloride, copper sulphate, cadmium and lead nitrates are similarly decomposed. On the other hand, it was found by Saget † that oxycellulose possessed a decreased affinity for the acid and phenol-like dyestuffs, notably Diamine blue 2 B and Erika B. Where colouring matters of this class have to be used in dyeing, the operation of bleaching with chloride of lime should consequently be omitted where practicable. With sulphide colours it dyes like ordinary cellulose. Of other properties of oxycellulose the following are characteristic:—It partly dissolves in caustic alkalies with a golden yellow colour, but if the amount present in the fibre is only small, the action only amounts to a tendering of the fabric. Its increased affinity for colouring matters and mordants is not destroyed either by washing with water, alcohol, alkalies, or acids, or by oxidising or reducing agents. Warmed with Fehling's solution, it reduces the latter with the formation of the characteristic red precipitate of cuprous oxide. When heated with hydrochloric acid it yields furfurol (Cross, Bevan, and Beadle). Its aldehydic character is further shown by its behaviour towards Schiff's reagent (Magenta decolourised by sulphurous acid), with which it yields a deep violet colouration. Phenylhydrazine colours it a deep yellow.

It should be borne in mind that most of these reactions apply to a highly oxidised cellulose, and many of them are not shown by cotton which has been but slightly converted into oxycellulose. The most delicate is the one originally suggested by Witz—viz., dyeing in a cold, dilute solution of Methylene blue.

Behaviour towards Mordants and Colouring Matters.—The cotton fibre has little or no affinity for ordinary metallic salts;‡ but when they are present in solution in a very basic condition, it is sometimes capable of decomposing them and loosely fixing the metallic hydroxides. Advantage is taken of this method of mordanting, especially in printing, the material being first padded or printed with a solution of some decomposable salts, like the acetates, and then aged. Thus if calico is padded in a solution of aluminium acetate, the alumina would be precipitated on the fibre in ageing, according to the equation—

$$Al(C_2H_3O_2)_3 + 3H_2O = Al(OH)_3 + 3C_2H_4O_2.$$

The only mordants which appear to have a direct affinity for the cotton fibre are the tannins (*q.v.*); and these are used in considerable quantities in cotton dyeing.

Up to the year 1884, the only dyes for which cotton showed a direct affinity were indigo, turmeric, safflower, and annatto. Some of the basic dyes, such as Safranine and Methyl violet, have, indeed, a slight affinity for cotton,§ and are used (when fastness is not a desideratum) for the production of light

* *Comptes rendus*, 1897, p. 448. † *Journ. Soc. Dyers and Col.*, 1892, p. 206.

‡ Lead forms an exception, being readily taken up by cotton from solutions of the acetate, the basic acetate or alkaline lead solutions.

§ Compare R. Haller, *Journ. Soc. Dyers and Col.*, June, 1907.

shades without the intervention of a mordant. But with the discovery of Congo red by Bottiger in 1884, the practice of cotton dyeing may be said to have entered upon a new era. The discovery of this new product was rapidly followed by numbers of others, commercially known as "benzidine dyes," "diamine dyes," "salt dyes," or "direct cotton dyes," with which we are at the present time able to produce almost any shade, except bright violets and bright greens. The majority of the direct cotton dyes are applied in an alkaline bath. The sulphide colours also evince a direct affinity for the cotton fibre.

Behaviour towards Micro-organisms and Ferments.—Certain micro-organisms completely destroy cellulose. Of the enzymes cytase has a similar action. Human saliva also appears to have the property of modifying the properties of cellulose, imparting to it an increased affinity for direct colours.*

FLAX, LINEN (Ger. *Flachs*, *Leinen*; Fr., *Lin*).

Linen, which is the product of the flax plant, ranks next to cotton in importance among the vegetable fibres. The flax plant most generally cultivated is the *Linum usitatissimum.* Flax thrives best in a temperate climate. The seeds are sown either in spring or in summer, the former yielding the finer quality.

In consequence of the tenacity with which the bast fibres of flax adhere to the woody portion of the stem, its separation is tedious and involves several operations. The first of these is the *retting*, the action of which depends upon a process of fermentation. It may be carried out in various ways, viz. :—

(1) By steeping in stagnant water;
(2) By steeping in running water;
(3) By exposure on fields (dew retting);
(4) By artificial means.

1. *Retting in stagnant water* is carried out chiefly in Russia and Ireland. It consists in steeping the flax in ponds or pits, from which the water can be let off when desired. The fermentation which takes place is accompanied by the formation of much soluble organic matter, and also by an intensely disagreeable smell. If care is not taken the fermentation is liable to become excessive and the fibre is weakened by overretting. The water used for this kind of retting should be soft, hard water being unsuitable. The retting is completed by exposing the flax in fields to atmospheric action for a week or so, a process which is known as *grassing.* Flax retted in this manner is of a dark colour.

2. The process of *retting by steeping in running water* is carried out principally in France, Belgium, and Holland. The flax is packed in large wooden crates and immersed in the running water. The fermentation sets in after a few days, when the flax is taken out, allowed to dry, and returned to the crates. The duration of the process varies from 10 to 20 days. Flax retted in running water is of a much lighter colour than that retted in stagnant water.

3. *Dew retting* consists in exposing the flax in a moist state in fields for periods extending to 10 weeks. The same kind of fermentation ensues as in the preceding process. Dew retting is used largely in Russia and Germany.

4. Of the numerous processes which have been brought forward from time to time with the object of *retting by artificial means*, none appear to have met with complete success. One of the simplest—viz., that of R. Baur—consists in

* Knecht, *Journ. Soc. Dyers and Col.*, 1905, p. 189.

first treating the flax for an hour with water acidulated with sulphuric acid and heated to 100° C. The pectic acid, which is thus converted on the fibre into a gelatinous condition, is then removed by treatment with a warm soda solution.

According to Beijerinck and van Delden,* the retting of flax involves essentially a fermentation of the pectose in the layers of cells above and below the system of bast fibres, whereby the latter are loosened. The specific bacterium which brings about this change in "water retting" is the *Granulobacter pectinovorum*, which excretes the enzyme *pectosinase*, and this in turn acts on the pectoses after the manner of a hydrolysing acid, converting them first into pectin and then later into sugars (probably galactose and xylose, but perhaps in some cases also glucose and arabinose). These undergo further fermentation with the production of hydrogen, carbon dioxide, and a little butyric acid. In "dew retting," the active agents are, according to Behrens, mould fungi. But certain aërobic bacteria, notably of the species of the group of hay bacilli (also known as potato bacilli), are likewise capable of effecting the retting of flax with full exposure to the air. In the case of the hay bacilli the sugars produced are not further fermented. The same authors find that the active retting bacteria are favoured by removing the soluble matters of the flax stems by changes of water in the early stages of retting.

From their researches on the subject, Beijerinck and van Delden recommend water retting in vats as the best practical process for the retting of flax. The flax is packed tightly in deep wooden vats provided with false bottoms. The quantity and temperature of the water can be thus controlled, and the water can be discharged for the purpose of aerating the goods and removing the lactic and other bacteria. The first steep-water containing the soluble matters should be discharged after twenty-four hours. The second steep should consist of a mixture of fresh water and good retting liquor from a previous operation. This may be replaced on the third day by fresh water since the true retting bacteria will then have become established.

The quality and the chemical composition of the flax vary considerably, according to the process used in retting. Thus, a flax retted by the Belgian process contained 82·5 per cent. of cellulose, and 7·6 of sugar; while one obtained by retting in warm water was found to contain 88 to 89 per cent. of cellulose, and only 1 to 2 per cent. of sugar.

After retting, the flax is subjected to several mechanical operations, the object of which is to remove the woody portions of the stem as completely as possible.

The first of these operations is the *breaking*, by which the woody portion of the stem is broken up so as to facilitate its removal in the next operation. Breaking may either be done by hand with the help of a simple contrivance, or by passing the stalks through a pair of fluted rollers.

In the next operation, that of *scutching*, the particles of wood are beaten out either by hand or by machinery.

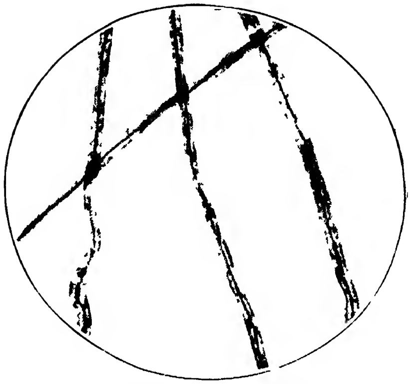
Next comes the process of *heckling*, the object of which is to lay the fibres parallel. This is effected by drawing the flax in bundles, first through coarse combs, then through finer and finer combs, until it is in a suitable condition for being spun. The combed or heckled flax is technically known as *flax-line*. The waste is technically known as *tow*.

Composition and Structure.—Although consisting, like cotton, essentially of cellulose, linen differs materially from the latter fibre in its physical properties. As they occur in the raw material, the individual or ultimate fibres are gummed tenaciously together, but by treatment with dilute chromic acid they can be separated. Under the microscope, these individual fibres are seen in

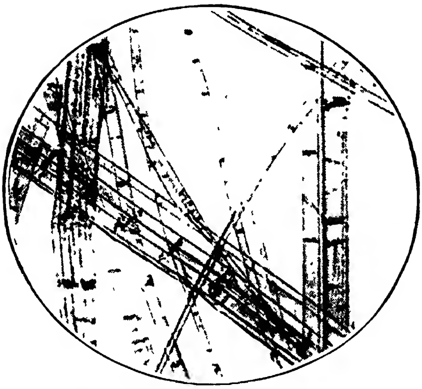
* *Mitth. Kgl. Akad. Wissensch.*, Amsterdam, 1903, p. 673.

Plate II.

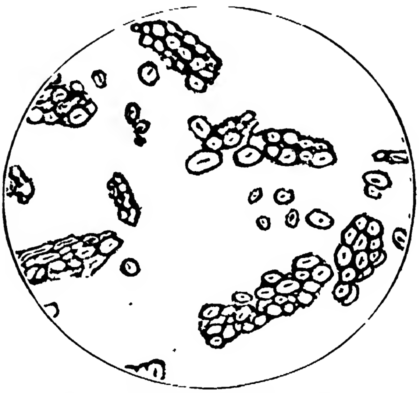
No. 7.—Egyptian cotton, mercerised under tension. × 60 diam.



No. 8. Egyptian cotton, mercerised without tension × 60 diam



No. 9.—Raw flax. × 60 diam.



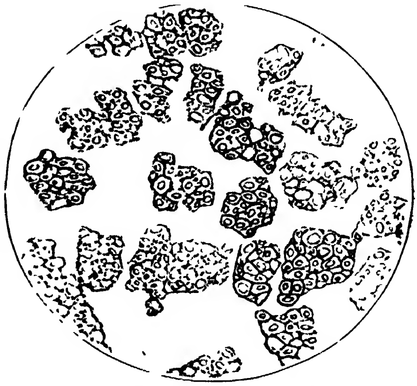
No. 10.—Raw flax (section). × 60 diam.

No. 11.—Bleached linen. × 60 diam.

No. 12.—Hemp. × 60 diam.

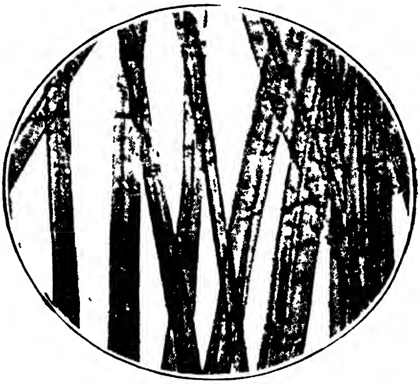
[*To face* p. 4

No. 13.—Raw jute. × 60 diam.

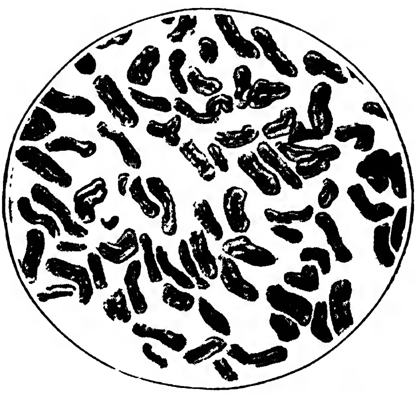


No. 14.—Raw jute (section). × 60 diam.

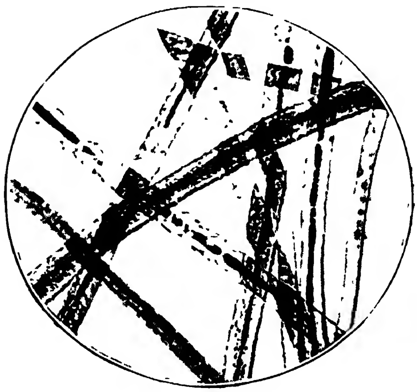
No. 15.—Jute breaking into ultimate fibres. × 60 diam.



No. 16.—China grass. × 60 diam.



No. 17.—China grass (section). × 60 diam.



No. 18.—Wool (Kent legs). × 60 diam.

[*To face* p. 43.

the form of long cylindrical vessels which terminate conically at each end. The cell walls are very thick, and the lumen is so small as to be indicated only by a thin black line. The mean length of the ultimate flax fibre is 20 to 40 mm., the breadth ranging from 0·012 to 0·026 mm., but generally the latter remains within the limits of 0·015 to 0·017 mm.

Flax is a better conductor of heat than cotton, and this is the reason why linen articles are colder to the touch than cotton. Besides, linen is stronger and more durable than cotton, and possesses a peculiar lustre. Air-dried linen contains 6 to 8 per cent. of hygroscopic moisture. As in the case of cotton, the strength of linen fabrics is increased by raising the percentage of moisture, and *vice versâ.**

Chemically, linen consists essentially of cellulose, but the amount of impurities contained in the raw flax is much greater than in raw cotton, varying from 15 to 30 per cent. by weight. In Schweizer's reagent, linen dissolves readily. Sulphuric acid and iodine colour it blue; sulphate of aniline has no action.

Towards chemical reagents generally, linen behaves like cotton. In bleaching it requires a longer and more complicated treatment, owing to the difficulty of removing the large amount of pectic and other substances which the raw fibre contains.

Towards the dyes and mordants, linen also behaves like cotton; but it is more difficult to dye than the latter. This difference is possibly due to the difference in the physical structure of the two fibres; according to another view, it is due to the presence of pectic substances in the linen.

Counts.—In linen yarn the counts indicate the number of *leas* to the pound. A lea consists of 300 yards.

HEMP (Ger., *Hanf*; Fr., *Chanvre*).

This fibre is the bast of the hemp plant, *Cannabis sativa*, which is cultivated in most temperate climates. The treatment of the hemp stalks is quite similar to that of flax, and includes rippling, retting, breaking, scutching, and heckling. Hemp is used principally for the manufacture of ropes, canvas, and sacking; for which purposes the fibre is eminently suited on account of its tenacity and the fact that it does not easily rot under water. It is seldom bleached or dyed; for, although this is possible, the fibre is too coarse to compare favourably with linen.

The ultimate fibres of hemp resemble those of linen in their appearance under the microscope, and have a diameter of 0·015 to 0·021 mm. The raw hemp fibre contains about 70 per cent. of pure fibre, the rest consisting of lignified or incrustaceous substances, wax, extractive matter, hygroscopic moisture, and ash.

JUTE.

Jute is the product of different species of *Corchorus*, plants indigenous to India. The most important species is the *Corchorus capsularis*, which is cultivated largely in most of the tropical climates of Asia.

When pulled the plants are stripped of their leaves, twigs, and fruit capsules, and are left lying for a few days in sluggish streams. This simple retting suffices to cause the bark to part from the stem, when it is stripped, rinsed in water, and dried in the air. The fibre thus obtained is very clean and comparatively pure. It comes into this country in the form of bundles. The length of the raw fibre is from 1½ to 2½ yards. About a foot of the

* See also *Journ. Soc. Dyers and Col.*, 1893, p. 203.

bottom ends is cut off, and forms, as jute butts or jute cuttings, a valuable material for paper-making. The rest, after having been softened with an emulsion of oil in soap, is heckled and spun.

The ultimate jute fibres, which can be readily isolated from each other by means of caustic potash or dilute chromic acid, consist of bast cells, which vary in length from 0·8 to 4·1 mm., and in diameter from 0·01 to 0·032 mm. The transverse section of these cells usually appears pentagonal or hexagonal, the lumen varying in size, from a large internal opening to a mere speck.

Jute differs considerably from the vegetable fibres hitherto considered, in its chemical composition and properties. It contains no free cellulose, but consists, according to Cross and Bevan, of a chemical combination of bastose and cellulose, to which these authors have given the name of *Corchorobastose.* This substance shows the reactions of lignified tissue; it is coloured an intense brown by sulphuric acid and iodine, and a dark golden yellow by sulphate of aniline. If treated with chlorine and then with sulphite of soda, the jute fibre is coloured a beautiful crimson; tanned cotton behaves in a similar manner. Jute absorbs chlorine and bromine with avidity, and becomes chemically changed; the ordinary process of bleaching with chloride of lime is, therefore, not well suited for this fibre. By heating with bisulphite of soda under pressure the tendency of the fibre to rot is considerably lessened, and it is also thus rendered less liable to become discoloured.

Action of Water.—According to J. R. Appleyard, both bleached and unbleached jute yarn lose weight when boiled in water, and, at the same time, a shrinkage and slight tendering are noticed.

According to the same authority, boiling for sixty minutes with 3 per cent. of its weight of sulphuric acid slightly tenders the yarn, and, further, has the effect of causing each fibre to become more brittle, thus deteriorating the quality of the material. Alum has little or no deleterious effect on the fibre, and is, therefore, recommended as an assistant in dyeing in place of sulphuric acid.

After treatment with sulphuric acid the bleached yarn has a more glossy and silky appearance, whilst the unbleached yarn is turned more of a pink colour.

According to Cross and Bevan, when jute is treated with 5 per cent. sulphuric acid, at a temperature of 80° to 90° C., it is slowly acted upon with the production of a body, soluble in alcohol, which is also a carbohydrate.

In dyeing, jute distinguishes itself by its natural affinity for the basic and some of the acid colouring matters. It is used largely in the manufacture of carpets, matting, sack-cloth, &c.

Counts.—For jute yarn, the counts are the same as for linen.

CHINAGRASS (GER., *Nessel;* FR., *Ramie*).

This fibre, also known under the name of Rhea or Ramie, is the bast fibre of a kind of nettle, botanically known as *Boehmeria nivea,* which is largely cultivated in China, India, and other countries.

The great difficulty in the production of this fibre lies in the fact that no entirely satisfactory method has hitherto been devised for separating the bast from the stem and bark. The process of retting as carried out with flax, hemp, and jute is not suitable, since, after a very short time, the bast is so completely separated into its ultimate fibres that the latter cannot be recovered coherently, but become so entangled with the other portions of the stem that their subsequent separation is practically impossible.

The usual process adopted is to separate the bast from the stems while the latter are still green. This can be readily effected by hand or by machine.

In that constructed for this purpose by Messrs. Death & Ellwood of Leicester, the green stems are pushed against a revolving beater which breaks the woody part of the stem. The removal of the broken wood and the washing of the raw fibre are effected by means of a powerful jet of water.

After standing for some time the fibre becomes so firmly attached to the woody portion of the stem that it cannot be completely detached, and, as this is almost inevitable in hot climates like India, various remedies have been recommended to counteract this evil. According to Favier the fibre may be readily separated from the dried stems by steaming them for 15 to 30 minutes in wooden boxes. Sansone recommends the treatment of the dried stems for 20 to 30 minutes in a boiling solution of carbonate of soda or of caustic soda, or the storing of the green stems in pits containing a solution of bisulphite of soda or sulphurous acid by which fermentation is prevented.

The individual fibres of the Chinagrass obtained from *Boehmeria nivea*, possess a maximum length of 22 centimetres and a diameter which varies from 0·04 to 0·08 millimetre. The raw fibre contains, according to Hugo Müller, 78 per cent. of cellulose and 6 per cent. of intracellular substances and pectic matter. In the purified state the Chinagrass fibre is characterised by its beautiful silk-like gloss, which is superior to that of linen. For the basic colouring matter it exhibits a slight affinity. Although easy to bleach, it is difficult to dye it in full bright shades without injuring the characteristic lustre of the fibre.

OTHER VEGETABLE FIBRES.

The most important vegetable fibres have already been mentioned; but a host of others are known, only a few of which are used in this country. The most important are:—Manilla hemp, Sunn hemp, Sida fibre, New Zealand flax, and the fibres obtained from the leaves of the aloe, the agave, the banana, the palm, and the fibrous material which surrounds the cocoa nut. As these fibres are seldom dyed, they will not be further considered in this work.

THE ANIMAL FIBRES.

WOOL (Ger., *Wolle;* Fr., *Laine*).

The hairs of the mammalia are cylindrical or conical shaped, horny, cellular structures. Each hair consists of a shaft and a bulb. The shaft is that portion which appears above the surface of the skin. If traced to the skin, it is found to be rooted in a follicle in the true skin, or even in the connective or cellular tissue beneath it. At the lower extremity of the follicle there is a small wart-like elevation, the hair papilla, from which the hair derives its nourishment. Each hair is connected with two or more cuticular glands which supply the follicle with fatty matter, serving to preserve the pliability of the hair, to protect it from outside influences, and to lubricate the epidermis. Down, wool, fur, bristles, &c., are all modifications of hair, differing from it only in their pliability, length, diameter, &c.

As a rule, hairs consist of three distinct tissues; the middle one is known as the medulla, which is surrounded by the cortex, a layer of horny substance, and this again by the outer or epithelial cells. One or other of these tissues may, however, be absent; thus, in down, the medulla is almost always absent, and the same frequently applies to bristles. In other cases the epithelial scales are sometimes rubbed off, and if the medulla is strongly developed, the

cortex is scarcely recognisable. The tenacity of a hair is in an inverse ratio to the relative thickness of the medulla; the greater the latter, the more brittle the hair. The tenacity and elasticity of hair depends chiefly on the relative amount of cortex and on the uniform structure of this constituent. The epithelial scales may either lie flat against each other, or may cover each other like the scales of a fish or the slates on a roof.

Strictly speaking, wool is the hair of the sheep, but the hair of certain goats—*e.g.*, Cashmere and Mohair—and of the camel are generally classed under the same category.

Some naturalists assume that there are only three original species of sheep, viz.:—

The *Ovis ammon* or argali, the wild sheep of Asia and America; the *Ovis musmon*, indigenous to the south of Europe and the northern parts of Africa; and the *Ovis aries*, or domestic sheep, which is the principal English variety.

From an industrial point of view, Archer distinguishes no less than 32 different varieties, of which 4 belong to Europe, 15 to Asia, 11 to Africa, and 2 to America. All these varieties give rise to different qualities of wool, which are distinguished from each other by the length, fineness, strength, elasticity, colour, curl, &c., of the fibres. The wool not only varies in quality with different animals, but also on one and the same individual. The best is that from the shoulders, the lower part of the neck, the back, and the upper part of the sides, while that which covers the head, tail, belly, and legs is of an inferior quality. The separation of the various qualities of wool from each *fleece* can only be done by hand, and the operation is known as *wool-sorting.*

The diameter of the wool fibre is, as a rule, proportional to its length—*i.e.*, the shorter the *staple*, the finer the fibre and *vice versâ.* The dyer usually distinguishes between the coarse and long-stapled *lustre wools*, most of which are produced in this country; and the finer *merino* wools, which are imported principally from Australia and the Cape, and go under the general name of *Botany* wool. *Cross-bred wool*, which is the product of the cross-bred sheep (English and merino), is largely imported from the Argentine Republic, and possesses properties which are intermediate between those of Botany and lustre wools. In addition to these, the following may be specially mentioned:—

The *Cashmere* wool of India, which is the produce of a goat which abounds in the mountains of Thibet. The hair of this animal sometimes reaches 18 inches in length.

Mohair, which is the wool of the Angora goat, is imported into this country chiefly from Turkey and the Cape. Mohair is characterised by its striking lustre.

Alpaca, the hair of an animal which belongs to a genus of which the Llama is the best known. Closely allied to this is the so-called *Vicuna wool*, of which, however, only very small quantities are available.

Camel's Hair.—The camels, which abound as domestic animals in many hot climates (especially in the northern parts of Africa), cast their hair periodically; this is collected, and comes into the market as a textile material.

Fur consists principally of the hair of the hare and the rabbit, and is extensively employed in the manufacture of better class felt hats.

The wool of diseased sheep, or such as have died from disease, is of inferior quality to that taken from the living animal. It also behaves differently in dyeing. Bosc gives an interesting account of an experiment carried out by him with the wool of three Rambouillet sheep, all of the same age and race. The first was in robust health, the second diseased, while the third had died of disease. Each fleece was washed separately and spun into yarn. The yarn was made up into hanks and dyed at the Gobelins in three shades, viz.,

blue, red, and yellow. The colours of the hanks made from the wool of the healthy sheep were bright, of the diseased sheep of a lighter shade, and those from the dead sheep dull. In dyeing each colour, all three samples were dyed in the same bath.

The wool from slaughtered sheep, if removed from the skin by cutting, is not inferior in quality to that shorn from the living animal. But the usual process for removing the wool from the skins is to steep the latter for a time in lime water or dilute solution of sodium sulphide. This causes the fibres to become so loosened at their roots that they can be readily removed. The wool obtained in this manner is generally known as "pulled wool," and is inferior in quality to that obtained from the living animal.

Wool comes into the market in different conditions; some has been washed on the sheep's back before the clip, but the greater portion of what is offered for sale is "in the grease." In either case it must be washed or scoured before it can be further dealt with.

According to its length of staple, wool generally is divided into long-stapled and short-stapled qualities. In the process of combing, to which most wools are subjected after being sorted and washed, before being spun, these fibres are separated. The long-stapled fibres (exceeding 1½ inches in length) are usually made up into *tops* (*slubbing*), and are spun, with the addition of about 2 per cent. of olive oil (English system), on ring- or cap-spinning frames, or, on the other hand, without the addition of oil, on mules (French system), into *worsted yarn*;* the shorter fibres, the so-called *noils*, are carded and spun on mule spinning frames into *woollen yarn*. Worsted yarn is used principally in the manufacture of worsted coatings and trouserings, braid, ladies' dress goods, &c., which require little or no milling. Woollen yarn, on the other hand, is used principally in the manufacture of goods which are subsequently milled for the purpose of producing to a greater or less degree a felting of the fibres. In worsted yarn, the fibres lie more or less parallel to each other, and the diameter of the yarn does not vary much, while in woollen yarn, the fibres lie pretty well in all directions, and the diameter of the yarn is very irregular.

Counts.—In worsted and Mohair yarns, the counts indicate the number of hanks of 560 yards each to the pound.

For woollen yarns they are different. In Yorkshire, the counts are generally the number of yards per dram, but in Dewsbury they indicate the number of yards per ounce. In the West of England the woollen counts indicate the number of hanks of 320 yards each to the pound.

Structure of the Wool Fibre.—When seen under the microscope, the cleansed and white wool fibre appears in the form of a solid rod-shaped substance, the surface of which is covered with broad scales, all projecting in the same direction, almost like the scales of a fish.

When the animal has been clipped for the first time (hog wool), the fibre tapers to a blunt point, but after the second and subsequent clips (wether wool), it terminates abruptly.

According to F. H. Bowman, the wool fibre consists of a vast number

* Most of the worsted yarn produced in this country is spun on the English system, and consequently contains oil which has been added with the object of facilitating the spinning, while that spun abroad, especially in France and Germany, contains no oil, as it is mostly spun on the French system. Before dyeing, goods made from English yarn must be well scoured, in order to remove the oil, but, however well this operation may be conducted, small quantities of the oil (probably oxidised or polymerised) are retained by the fibre. This fact largely accounts for the statement so frequently made that worsteds can be dyed on the Continent better than here. In place of olive oil, Turkey-red oil is sometimes used for oiling wool, and recently Markel has patented the use of ricinoleic acid for the purpose.

of individual cells which taper towards each end to a finer point. Their number in a transverse section may exceed 1,500. The central or medullary cells are generally somewhat larger than those immediately surrounding them; and, in the case of black or coloured wool, contain the organic pigment to which the wool owes its colour. The outer, or epithelial cells are flat, horny, shield-shaped discs, which overlap each other (Figs. 1 to 3*c*). These cells can be made to stand out more prominently by treating the wool with sulphuric

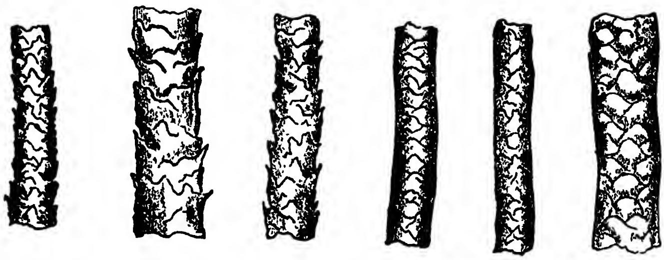


Fig. 1. Fig. 2*a*. Fig. 2*b* Fig. 3*a*. Fig. 3*b*. Fig. 3*c*.
Microscopical appearance of various wool fibres (*Bowman*).

Fig. 1, Fine merino. Fig. 2*a*, Lincoln wool taken from the coarsest part of the fleece after treatment with caustic soda and washing with alcohol and water. Fig. 2*b*, Lincoln wool taken from the shoulders of the same fleece as 2*a*. Fig. 3*a*, Alpaca. Fig. 3*b*, Mohair. Fig. 3*c*, Coarse hair from Cheviot fleece.

acid, or, better still, by steeping the fibres for two to three minutes in strong ammonia. Their presence also makes itself evident without the aid of a microscope; for, if a single wool fibre or a hair is taken between the finger and thumb of each hand and drawn gently, the end nearest the root remains stationary while the other slips. This simple experiment is instructive as showing the behaviour of wool in the process of *milling*. In the "drawing" of wool for worsted yarns, as also in the carding and drawing for woollen yarns, the result of the operations is that about 50 per cent. of the fibres lie in one direction and 50 per cent. in the other. If worsted or woollen

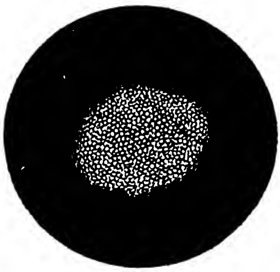
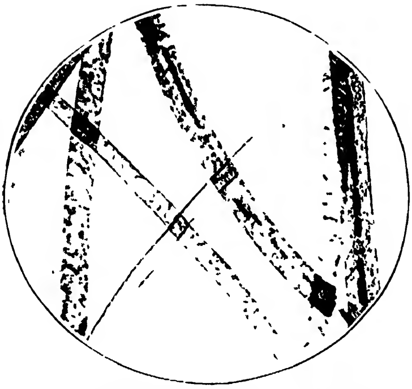


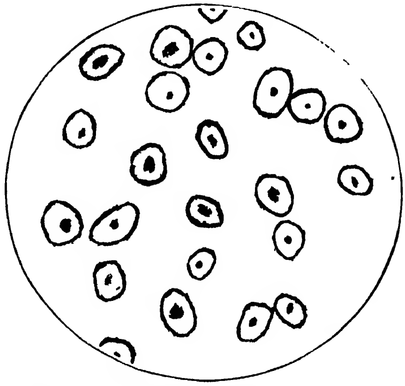
Fig. 4.—Transverse section of wool fibre (*Bowman*).

fabrics are subjected to friction in the wet state, especially in presence of an alkali (soap or soap and soda), the friction of the fibres against each other is greater in one direction than in the other, and the consequence is that the fabric contracts or "runs" or "felts," becoming at the same time thicker and assuming a denser appearance. The object of *milling* is to produce this effect. The process is used in the manufacture of flannels, broadcloths, tweeds, and other classes of woollen goods. As soap is generally used to accelerate its action, the colours used in dyeing the wool or the yarn for all but plain goods must be fast to soap, and should not run or bleed. In the dyeing of slubbing and yarn, this property of felting is a

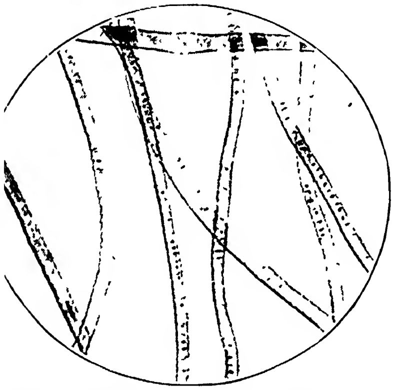
Plate IV.



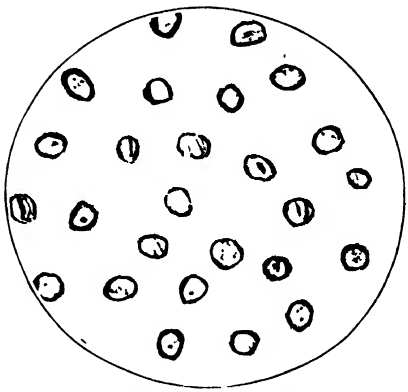
No. 19.—Wool (Lincoln hog). × 60 diam.



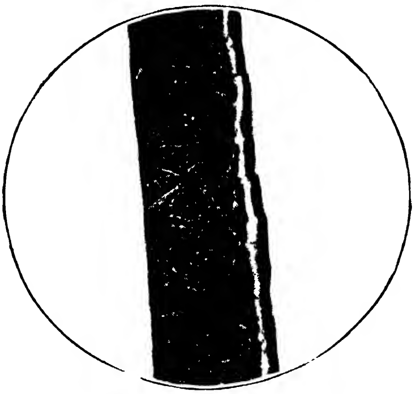
No. 20.—Lincoln hog (section). × 60 diam.



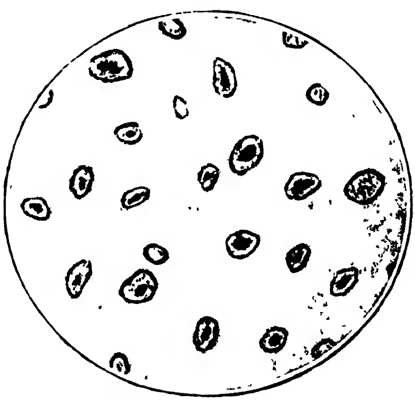
No. 21.—Wool (Botany Bay). × 60 diam.



No. 22.—Wool: Botany Bay (section). × 120 dian



No. 23.—Kempy wool. × 120 diam.



No. 24.—Kempy wool (section). × 60 diam.

[*To face p.* 48.

drawback, and careful treatment of the material is necessary in order to avoid its occurrence. In the production of felt from rabbit's fur, the fibres are specially treated with nitrate of mercury in order to make them felt well.

In section the wool fibres are generally round or elliptical, and exhibit a number of ducts through which the nourishment is possibly furnished.

The length and diameter of the individual wool fibres vary considerably, not only according to the origin, but also in one and the same fleece. As stated above, the diameter is usually proportional to the length. The average length of the various classes of wool may be taken as varying between 1½ and 7 inches, and the diameter from 0·004 to 0·0018 inch. The following figures are taken from Bowman's *Structure of the Wool Fibre*:—

Kind of Wool.	Breaking Strain in Grains.	Elasticity in Percentage of Length.	Diameter of Fibre in Decimals of an Inch.
Leicester Wool, ...	502	0·284	0·00181
Southdown Wool, ...	86	0·268	0·00099
Australian Merino, ...	50	0·335	0·000[illegible]17
Saxony ,, ...	39	0·272	0·000338
Mohair, ...	586	0·299	0·00170
Alpaca, ...	149	0·242	0·000526

In the coarse qualities of wool, and especially in mohair, fibres are frequently met with which strike the eye by their characteristic ivory-white appearance. Under the microscope these fibres are seen to be void of internal structure, they do not felt, and in dyeing come out considerably lighter than the other fibres of the same wool. They are technically known as *kemps*, and, although they are usually eliminated to a great extent in the process of combing, those which remain may be a source of annoyance to the spinner, manufacturer, and dyer alike. It does not always happen that the whole fibre is kempy. It may be healthy up to a certain point and thence kempy to the end, or even kempy in the middle and healthy at both ends.

In their chemical composition, kemps do not appear to differ from the healthy fibres, and their different behaviour in dyeing must be due to the horny impenetrable nature of the fibre.

The difficulties experienced in the dyeing of goods containing kemps may be overcome to a great extent by chlorinating (*q.v.*), the use of a high temperature in the dye-bath, and the choice of suitable dyestuffs. Ladies' dress goods have, however, been in fashion in which white fibres show on a coloured ground, and kemps were used for this purpose to such an extent that the demand became greater than the supply, and their market value soon exceeded that of the wool and mohair from which they were separated. Methods were also patented for so treating ordinary wool as to render it incapable of taking up colouring matter.

Physical Properties.—Wool is hygroscopic, and to a much greater extent than the vegetable fibres. When dried at 100° C. wool loses on an average 18·25 per cent. of moisture,* and this is the amount officially allowed. When the dried wool is freely exposed to the air, this amount is regained in a comparatively short time. But the amount of moisture held by the wool may be considerably less than or in excess of this figure according to the temperature and hygrometric condition of the atmosphere in which it has been kept. In

* By this it is meant that 118¼ lbs. of wool in the normal condition yield 100 lbs. of dry fibre (*shrinkage*), or that 100 lbs. of perfectly dry wool will increase in weight to 118¼ lbs. if freely exposed to the air (*regain*). With other textile fibres the calculation is similar.

4

fairness, therefore, to both buyer and seller, conditioning houses have been established in all the most important worsted and woollen manufacturing centres of the Continent, and, subsequently, also in Bradford, in which the wool is sampled and tested for the amount of hygroscopic moisture and oil which it contains. The *modus operandi* is similar to that used in conditioning silk (*q.v.*).

Wool dried at 100° assumes a harsh feel and its strength becomes considerably diminished. When exposed to temperatures above 110°,* the wool fibre begins to become affected, while at 130° a more or less complete decomposition of the fibre sets in. This can be avoided, according to Persoz, by previously impregnating the material with a 10 per cent. solution of glycerin. After this treatment it can be exposed without alteration to a temperature of 130° to 140°.

At 100°, wool containing its normal amount of moisture becomes plastic, and can be made to assume in this condition almost any shape which may be given to it, which shape it retains afterwards, if the material is allowed to cool in the same position. This property of the wool fibre is of the greatest importance in the crabbing and hot finishing of piece goods and in the stretching of yarns. The same principle is applied in the production of curled worsted yarn, such as is employed in the production of imitation astrachans and of fancy yarns. Curled yarn is produced by twisting the wool tightly, boiling for some time in water and then cooling. This sets the yarn in its twisted condition, and gives it a permanent curl. With horn, which is morphologically and chemically closely allied to wool, the property may be readily demonstrated by plunging a spatula or paper knife of this material for a few minutes into boiling water. When taken out it is quite limp, and can be readily bent in any direction. If it is now bent double and plunged in this position into cold water, it retains the shape that has been given to it, and cannot be bent straight again while cold.

Chemical Properties of the Wool Fibre.—Chemically, the wool fibre differs from all others in its composition and properties. When it comes from the sheep's back, the fibre is in a very impure condition, being contaminated with a large amount of grease (yolk) and dried-up sweat (suint). These constituents will be noticed again under wool-washing. When thoroughly cleansed the wool fibre is found to be composed of carbon, hydrogen, oxygen, nitrogen, and sulphur, but as these elements (especially the sulphur) not being present in constant proportions, it is not possible to assign to wool a definite chemical formula. It consists of keratine, a proteïd substance, the constitution of which is little known, but which constitutes not only the wool fibre, but all horny tissues, such as hair, horn, whalebone, feathers, &c.

The average composition of wool-keratine may be taken as—

Carbon,	50·00 per cent.
Nitrogen,	15-17 ,,
Hydrogen,	7·00 ,,
Sulphur,	2-4 ,,

the difference between the sum of these figures and 100, being oxygen. The amount of sulphur, which usually averages from 2 to 4 per cent., may even exceed these limits considerably. Thus wools have been examined which have contained as little as 0·8 per cent., while Bibra found in some red human hair which he examined no less than 8·23 per cent. The sulphur contained in wool seems to be of two kinds, one of which may be removed by prolonged treatment with alkali, while the other cannot. By successive treatments with lime-

* Bowman maintains that continued heating to 100° C., or even less, brings about a permanent alteration in the fibre.

water, water and hydrochloric acid, Chevreul succeeded in reducing the amount of sulphur in one case to 0·46 per cent. Wool dissolved in caustic soda and then treated with dilute acid gives off about 70 per cent. of the sulphur originally present, as sulphuretted hydrogen.

The presence of sulphur in wool can be readily shown by heating the material in a diluted solution of lead oxide in caustic soda. The fibre soon turns brown and ultimately black, owing to the formation of lead sulphide Advantage is taken of this reaction for readily distinguishing wool from other textile fibres, for the production of cheap (but injurious) hair-dyes, and for making imitation tortoise-shell from ordinary horn. On the other hand, the presence of sulphur in wool is not without its drawbacks, as will be seen from the following series of dyeing experiments carried out by Rawson.*

The colouring matters taken were the following:—Naphthol yellow, Tartrazin, Manchester yellow, Brilliant green, Safranine, Magenta, Rhodamine, and Night blue. The only natural colouring matter experimented upon was indigo, which was dyed in the form of indigo-sulphonic acid. Some of these colouring matters were dyed in a neutral bath, and others with addition of sulphuric acid. The experiments were made in a series of four. In the first place the water used was free from lead, in the second $\frac{1}{3}$ grn. of lead per gallon was added, in the third $\frac{2}{3}$ grn., and in the fourth 1 grn. per gallon. Wherever sulphuric acid is used in dyeing the colour is not affected by lead, but shades dyed in a neutral bath are rendered duller in proportion to the amount of lead present in solution. Wool treated neutral and with acid, without addition of colouring matter, behaved in a similar manner. In a neutral bath containing lead the wool was dyed a drab shade, but with addition of a small quantity of sulphuric acid ($2\frac{1}{2}$ per cent. on the weight of the wool) it remained white. In the case of Rhodamine, one of the brightest of all colouring matters, 5 per cent. of alum was used in the dye-bath, and the shade was almost, but not entirely, unaffected by the presence of lead. In the case of Night blue, the colour was dissolved in acetic acid, but the shade was affected in a similar manner to those dyed neutral. It is true that the amount of acetic acid present in the dye-bath would be exceedingly small, and the effect of a larger amount was not tried. The saddening effect is apparently caused by the sulphur naturally present in the wool combining with the lead, and forming sulphide of lead. But the formation of sulphide of lead on the fibre does not take place in the presence of sulphuric acid

In mordanting wool with stannous chloride, the material sometimes blackens, presumably through the formation of stannous sulphide. A similar action sometimes takes place, according to Hummel, in the formation of black specks in dyeing Cochineal scarlets on woollen cloth. According to others, these spots are due to the presence of metallic iron in the material. In an alkaline condition, wool is readily affected by metals, and for this reason wool which has undergone an alkaline treatment should never be brought in contact with metals before it has been thoroughly washed.

By dissolving wool in caustic soda, or in barium hydrate, there are formed, along with ammonia and sulphuretted hydrogen, a variety of organic compounds which are mostly amido-acids. One of the most interesting decomposition products is lanuginic acid, which was first prepared by Champion,† and was subsequently subjected to a more careful examination by Knecht and Appleyard.‡ It may be obtained by dissolving wool in boiling barium hydrate solution, removing the barium by means of carbonic acid, precipitating the lanuginic acid with basic lead acetate, and decomposing the lead salt with sulphuretted hydrogen. The solution filtered from the lead sulphide leaves, on

* *Journ. Soc. Dyers and Col.*, 1889, p. 161. † *Comptes rendus*, vol. lxxii., p. 330.
‡ *Journ. Soc. Dyers and Col.*, 1889, p. 71.

evaporating to dryness, the lanuginic acid as brownish-yellow, translucent, and amorphous substance which yields, on grinding, a cream-coloured powder, readily soluble in water. The aqueous solution possesses the remarkable property of precipitating the acid colours in presence of dilute sulphuric acid and the basic colours in the absence of free acid, forming intensely coloured lakes, most of which melt on heating. Tannic acid, bichromate of potash, and the acetates of aluminium, chromium, iron, and copper also yield precipitates. At 100° lanuginic acid becomes soft and plastic; at higher temperatures it swells up, turns brown, and gives off a smell similar to that of burning wool. The mean of two analyses of lanuginic acid gave the following figures:—

Carbon,	41·61	per cent.
Hydrogen,	7·31	"
Nitrogen,	16·26	"
Sulphur,	3·35	"
Oxygen,	31·47	"
	100·00	"

From more recent investigations by R. Gnehm * it would appear that the lanuginic acid prepared by Champion's method is not a uniform substance.

The property which lanuginic acid possesses of precipitating both colouring matters and mordants is of importance, as showing that a substance can be obtained from wool which is soluble in water, and which behaves towards colouring matters and mordants like the fibre itself. A similar body is obtained by the action of acids, as well as by the action of water at high temperatures, on wool. Furthermore, Reychler † showed that even the aqueous extract of wool contained a substance which was capable of yielding precipitates with the basic colours.

The presence of amido-nitrogen in wool was shown by P. Richard, ‡ by diazotising the fibre and combining with phenols, when azo-colours resulted. According to Bentz and Farrell, § wool treated with nitrous acid shows in every respect the characteristics of a diazo-compound. It gives the reactions of Griess and of Sandmeyer, and can, by treatment with stannous chloride, be reconverted into ordinary wool, which can be diazotised afresh. The amount of nitrogen which can be diazotised is, however, only 1 to 1·2 per cent.—*i.e.*, about $\frac{1}{15}$ to $\frac{1}{12}$ of the total nitrogen present. According to these authors the amido-nitrogen is not of importance in the dyeing process, since wool which has been completely deprived of its diazotisable nitrogen by boiling the diazo-compound with water, alcohol, or cuprous chloride, until it no longer reacts with nitrous acid, can be dyed just as well with acid (and basic) dyes as ordinary wool. This observation does not, however, preclude the possibility of the amido-group entering into the composition of the colour lake in untreated wool; it simply shows that the amido-group is not essential in dyeing.

In a series of carefully conducted experiments, Watson Smith ‖ showed that when wool is boiled in a solution of ammonium sulphate, considerable quantities of ammonia are liberated. By boiling 10 grms. of wool for four hours with 10 grms. ammonium sulphate in 100 c.c. water, he found that 0·0833 grm. NH_3 was liberated, while wool alone evolved 0·0020 grm., and ammonium sulphate alone 0·0272 grm. of ammonia under the same conditions. The amount of ammonia liberated by the action of the wool was, therefore, 0·0541 grm. Wool which has been boiled with ammonium sulphate (10 per cent. of the weight of

* *Journ. Soc. Dyers and Col.*, 1902, p. 142. † *Bull. Soc. Chim. de Paris*, 1897, p. 449.
‡ *Bull. Soc. Ind. de Mulhouse*, Sept. 1888. § *Journ. Soc. Chem. Ind.*, 1897, p. 406.
‖ *Journ. Soc. Chem. Ind.*, 1896, p. 246.

the wool) can be dyed without additions with the acid colours. The action of the so-called metachrome mordant (chromate of potash and ammonium sulphate) is probably due to a similar phenomenon.

According to C. Schoen,* the basic properties of the wool fibre are considerably weakened by treatment with metatungstate of soda, while at the same time its acid properties are enhanced, inasmuch as it has but little affinity for the acid colours, but a greatly increased affinity for the basic colours.

Under certain conditions wool may play the part of a reducing agent, and this property is shown especially with regard to Aniline black and some of the poly-azodyes. Possibly this is due to the presence of sulphur in the form of sulphuretted hydrogen. By oxidising the wool with chlorine or other oxidising agents, or by the addition of some oxidising agent to the dye-bath, this drawback may be overcome.

The ash of cleansed wool amounts, as a rule, to less than 1 per cent. by weight of the original material, and about three-quarters of it is soluble in water. The following analysis, by W. H. Wood, of the ash of Lincoln wool may be taken, according to Bowman, as typical:—

Potassium oxide, K_2O,	31·1	per cent.
Sodium ,, Na_2O,	8·2	,,
Calcium ,, CaO,	16·9	,,
Alumina, Al_2O_3, / Ferric oxide, Fe_2O_3,	12·3	,,
Silica, SiO_2,	5·8	,,
Sulphuric acid, SO_3,	20·5	,,
Carbonic acid, CO_2,	4·2	,,
Phosphoric acid,	trace.	
Chlorine,	trace.	
	99·0	,,

The ash of a scoured flannel was found by Fürstenhagen and Appleyard to be alkaline.† The alkalinity was due to

Lime,	0·094 per cent., calculated as	CaO;
Potash and soda,	0·224 ,, ,,	K_2O.

Action of Water.—The wool fibre consists of a horny transparent or translucent mass, which is not soluble in any of the ordinary solvents. At the same time, the fibre (even when well washed) is, to a certain extent, water-repellant, and, consequently, difficult to wet out. To thoroughly wet it, treatment with hot or boiling water is advisable.

By prolonged boiling with water, the wool fibre is gradually affected; ammonia and sulphuretted hydrogen are given off, and the wool loses both in lustre and tensile strength, while small quantities of a substance to which Gardner has given the name "wool gelatine" pass into solution. Acidulated water has less action on the fibre than pure water. When wool is steamed at 99° to 100° it is much more rapidly attacked than cotton, suffering a loss in strength, according to O. Scheurer,‡ amounting to 18 per cent. in the first three hours and to 75 per cent. in 60 hours. Wool which has been steamed shows an increased affinity for dyestuffs, and advantage is taken of this fact in the treatment of certain classes of mohair previous to dyeing. In the steaming of piece goods after crabbing, the same action occurs and may sometimes give rise to what are known as "ended" goods, so called because one end dyes darker than the middle. This is due to those portions of the goods which come nearest to the perforated roller having received a more drastic treatment than the rest of the piece.

* *Bull. Soc. Ind. de Mulh.*, December, 1892.

† *Journ. Soc. Dyers and Col.*, 1888, p. 104.

‡ *Ibid.*, 1894, p. 55.

Heated with water to 130° C., the wool fibre is so deeply attacked that it can, after drying, be rubbed to a fine powder. Silk is not materially affected by this treatment, so that it is possible by means of it to "carbonise" wool in presence of silk. Heated with water to 150° to 200° C., wool is completely dissolved.

Under the influence of moisture and a moderate heat, the wool fibre is apt to *mildew*, and this gives rise to faults. Such faults are met with especially in woollen cloths which have been soaped, milled, or vat-dyed, and are allowed to lie for some time in an alkaline condition. They may, however, also occur during the process of weaving, and have been known to form in summer time in less than twenty-four hours. By the action of mildew, the wool fibre is attacked or destroyed, and the spots or stains have little affinity for dyestuffs, showing as light places in the dyed material. According to K. Schimke,* the affected fibres are readily recognised under the microscope; they appear to be split up into individual fibrillæ, and show an appearance like a paint brush.

Behaviour towards Acids.—Dilute acids have little appreciable effect on wool, although, at a boiling heat, they are absorbed and retained by the fibre with great tenacity. The amount of sulphuric acid absorbed from boiling solutions, using 500 c.c. of liquid to 5 grammes of wool, was found by Fürstenhagen and Appleyard † to be as follows :—

Amount of Acid Employed.	Acid Left in Solution.	Acid Absorbed.	Indicator.
2½ per cent.	0·38 per cent.	2·12 per cent.	Methyl orange.
5 ,,	2·17 ,,	2·83 ,,	,,
10 ,,	6·37 ,,	3·63 ,,	,,
20 ,,	15·87 ,,	4·13 ,,	,,
40 ,,	35·18 ,,	4·82 ,,	,,

The acid thus absorbed cannot be readily extracted by boiling. Thus, wool which had been mordanted with 5 per cent. of sulphuric acid gave up to distilled water when boiled for an hour (500 c.c. water to 5 grammes wool), the following amounts :—

First boiling, ...	0·84 per cent.
Second boiling, ...	0·34 ,,
Third boiling, ...	0·08 ,,
	1·26 ,,

Further treatments continue to extract small quantities of free acid, but a not inconsiderable portion appears to be permanently absorbed or neutralised by the fibre. It is a remarkable fact that wool, which has been boiled with—say 10 per cent.—sulphuric acid, and then extracted repeatedly with water until the reaction is neutral, can be dyed in a neutral bath with the acid colours, which otherwise require a considerable amount of acid in the dye-bath. Benzene sulphonic acid acts in this respect like sulphuric acid.‡

Wool treated with dilute sulphuric acid loses none of its valuable properties, its strength, lustre, milling or felting properties, &c., remaining unimpaired. On the contrary, an acid treatment, if not too drastic, gives to the fibre additional "spring."

Sulphurous acid is also absorbed and retained tenaciously by the fibre; and in the case of yarn which has been stoved for the purpose of bleaching, the

* *Färber Ztg.*, 1891-92, p. 339. † *Journ Soc. Dyers and Col.*, 1888, p. 104.
‡ *Journ. Soc. Dyers and Col*, 1904, p. 244.

sulphurous acid retained by the wool may either retard the fixation of certain colouring matters or cause them to fade after dyeing or printing, owing to its reducing action. When stoved yarns are used along with dyed yarns in coloured fancy goods, the same effect may be produced at the crossing of the white and coloured threads.

From dilute aqueous solution, *hydrochloric acid* is absorbed like sulphuric acid. *Tartar* is decomposed by wool, according to Bolley, neutral tartrate being left in solution, while tartaric acid is retained by the fibre.

Dilute *nitric acid* when applied at boiling temperature is liable to turn the wool yellow. The colour thus produced is said to be due to the formation of *xantho-proteïc acid.* But, if the strength does not exceed 3° to 4° Tw., the formation of this compound takes place very slowly. Acid of this strength is frequently used by job-dyers, and, in shoddy dyeing, for "stripping" colours.

A. J. Perold has studied the behaviour of wool towards a large number of acids,* and shows that their absorption by the fibre is a chemical process.

Concentrated mineral acids completely destroy and dissolve the wool fibre. The action is, however, only instantaneous (or nearly so) in the case of nitric acid. Wool treated for a few minutes with concentrated sulphuric acid and then well washed is deprived to a considerable extent of its power of combining with dyestuffs.† When dissolved in strong sulphuric acid, wool yields a product which has the property of forming insoluble precipitates (lakes) with the acid colours. A similar compound is produced when wool is dissolved in strong hydrochloric acid; but in this case the action is slower. Nitric acid dissolves wool with copious evolution of nitrous fumes. The solution has an intense yellow colour. According to Raikow,‡ wool is almost completely dissolved on being allowed to stand for a prolonged period with syrupy phosphoric acid at the ordinary temperature. The composition of the degradation products was not determined, but it is interesting to note that, under these conditions, there is a copious evolution of sulphur dioxide.

Behaviour towards Alkalies.—Although proof against the action of even moderately diluted acids, wool is very easily acted upon by alkalies. The most powerful in this respect are the caustic alkalies and the hydrates of the alkaline earths. Their action varies, however, greatly according to temperature and strength of solution. At 0° the action of even concentrated caustic alkalies on wool is only slight, but, as the temperature increases, their action becomes more and more intense, until, at the boiling temperature, wool can be completely dissolved by prolonged treatment in a solution containing less than 1 per cent. of caustic soda calculated on the weight of the material.

When, however, wool is exposed to the action of very strong caustic soda, a phenomenon is observed which is similar to that which takes place in the mercerising of cotton. A. Kertecz § first noticed this, and made use of the increased affinity acquired by the wool for colouring matters for the production of two depths of the same colour in the printing of woollen fabrics. Buntrock ‖ further investigated the subject, and found that wool treated with caustic soda at 71° to 106° Tw. at the ordinary temperature was strengthened during the first five to ten minutes; beyond this time the tensile strength diminished. The best strength was found to be 82° Tw. Weaker caustic attacked the fibre more or less, and the destructive action was found to be strongest at 32° Tw.; both stronger and weaker liquors had less action.

In the cold, strong solutions of the caustic alkalies have little or no shrinking effect on either wool or silk, while cotton shrinks under the treatment some 20 per cent. On this difference in the properties of the fibres Depouily based

* *Journ. Soc. Dyers and Col.*, 1905, p. 171.
† *Ibid.*, 1903, p. 71.
‡ *Ibid.*, 1905, p. 274.
§ *Färber Ztg.*, No. 2, 1898.
‖ *Färber Ztg.*, No. 3, 1898.

a process of producing crimp or crape effects on fabrics consisting mainly of wool or silk, but containing in the warp or weft, or both, cotton binding threads. The fabrics are passed through caustic soda cooled to 0° to 10° C., washed in water, then in dilute acid, and again in water. By the contraction of the cotton threads the wool or silk assumes a crumpled appearance, and a great variety of effects can thus be obtained, which can be varied by the make of the cloth.

Wool has the property of absorbing caustic alkalies from dilute aqueous solution, as it does acids, but it does not retain the alkali so tenaciously as it does acids.

Alkaline carbonates exercise a destructive action on wool, although to a far less degree than the caustic alkalies. In dilute aqueous solution, and at moderate temperatures, they are often used along with soap for scouring wool and in milling. As a rule, no injurious effect is observed under these conditions, but it is well to bear in mind that their deteriorating effect increases with the strength of the solution, and more especially with the temperature; in comparatively dilute boiling solution of sodium carbonate wool is readily tendered, and by prolonged action it is completely disintegrated. The milder alkalies, like soap, borax, phosphate of soda, &c., have much less action on the wool fibre. The use of borax is resorted to when it is necessary to boil the wool in an alkaline bath, as, for instance, in the dyeing of Alkali blue. Ammonia and ammonium carbonate are also comparatively uninjurious when used in dilute solutions. Wool treated with formaldehyde is said to lose its sensitiveness to alkalies.*

Behaviour towards Oxidising Agents.—Boiled in a solution of permanganate of potash, wool rapidly turns brown, and the fibre is easily tendered, but the action is probably due as much to the liberated caustic potash as to that of oxidation.

By moderate treatment with permanganate of potash, J. Mullerus † found that wool acquired an increased affinity for colouring matters, its felting properties being at the same time diminished. Treatment with barium peroxide, followed by a treatment with acid, produced a similar effect. Chromic acid also exercises an oxidising action on wool, diminishing its tensile strength and impairing its felting properties. So-called "overchromed" wool owes its property of not taking a logwood black, according to Hummel, rather to the presence of an excess of chromic acid in the fibre than to any change in the substance of the fibre (see *Chrome Mordants*).

The beneficial action of chlorine and of chromic acid on the colour reception properties of wool was first recognised by John Mercer, who had experienced (previous to 1848) considerable difficulty in obtaining, in the printing of delaines, the same shade of colour on the wool and the cotton. He concluded that the difference in the absorbing power arose from the presence of some deoxidising agent in the woollen fibre, and discovered that by passing the material through a mixture of bleaching powder and hydrochloric acid the woollen fibre is rendered capable of combining with Prussian blue, oxide of tin, and colouring matters with the same facility as cotton, giving "full, rich, saturated colours." ‡ For woollen goods which are intended to be printed Mercer's process has been used ever since it was first introduced. After chlorinating, the goods are now usually stoved and then, according to the suggestion of G. Lunge, run through peroxide of hydrogen. The first of these processes takes away the yellow tinge produced by the chlorination, and the second destroys the sulphurous acid fixed by the wool.

* *Journ. Soc. Dyers and Col.*, 1903, p. 297. † *Ibid.*, 1892, p. 111.

‡ *The Life and Labours of John Mercer*, by E. A. Parnell (Longmans, Green & Co.), 1886, p. 86.

Dry chlorine exerts little or no action on dry wool,* whereas if moist chlorine gas is allowed to act on wool containing its natural amount of moisture, the fibre first becomes yellow, and is ultimately converted into a translucent viscous mass, while at the same time volumes of hydrochloric acid gas are liberated. The product thus formed has not been obtained in a pure condition, but resembles lanuginic acid, inasmuch as it is soluble in water, and the aqueous solution is capable of yielding lakes with colouring matters. Wool also greedily absorbs chlorine from aqueous solution without any material change taking place in the outward appearance of the fibre. According to Knecht and Milnes, wool treated (chlorinated) with bleaching powder and excess of hydrochloric acid contains no chemically combined chlorine, but owes its altered properties entirely to oxidation. Spotted with iodide of potassium solution, it is stained brown by separation of iodine even weeks after the treatment, but it was not ascertained whether this reaction was due to the presence in the fibre of free chlorine or of peroxidised products of the substance of the fibre. Wool chlorinated, as on the large scale for printing, was found to still contain that modification of sulphur which is blackened by alkaline lead solution, and the reaction with lead only disappeared at a point when the fibre had been partially disintegrated. Hypochlorous acid turns wool yellow much more rapidly than free chlorine. The yellow colouration can be removed by treatment with sulphurous acid, but the colour returns on steaming.

Chlorinated wool differs from ordinary wool in several important points. It has a better lustre, and in certain qualities a feel like that of scroop silk (silk-wool). On the other hand, its felting properties are either considerably diminished or altogether destroyed. That a chemical change has been brought about in the substance of the fibre is shown by its increased affinity for many colouring matters, and the fact that with the same percentage of dyestuff it is dyed a deeper shade than ordinary wool. Mercer † ascribed the fact that Prussian blue could be printed on chlorinated wool and developed as readily as on cotton to the destruction by the chlorine of reducing substances in the fibre, while Bethmann ‡ maintains that, as far as the successful production on the fibre of Aniline black is concerned, the chief point is to neutralise the basic properties of the fibre.

For the chlorination of wool on a large scale, 2 to 5 per cent. of bleaching powder is usually employed on the weight of the wool under treatment. In place of bleaching powder and hydrochloric acid Bulard § recommends the use of hypochlorite of soda and sulphuric acid, which, according to this author, is less liable to turn the wool yellow. To get over the necessity of chlorinating wool for printing, F. Bayer & Co. ‖ recommend the addition to the printing colour of bromates along with a suitable carrier of oxygen, such as vanadium chloride, or then to treat the wool with bromate and hydrochloric acid (separately or mixed). Bromine exerts on wool a similar action to chlorine (C. Schoen).

The peculiar action of chlorine in imparting a silk-like lustre to the wool fibre and of destroying its felting properties has been used extensively with the object of producing a kind of knitting wool known under the name of *silk-wool*, on the one hand, and for rendering hosiery, flannel, &c., unshrinkable, on the other. By chlorinating alone most kinds of wool assume a somewhat harsh feel, but can be rendered soft again by treatment with fatty acids.

For the production of silk-wool Lenzen ¶ gives the following recipe for knitting yarn:—The yarn is first treated for 15 to 30 minutes in a cold bath

* Knecht and Milnes, *Journ. Soc. Dyers and Col.*, 1892, p. 41.

† *Life and Labours of John Mercer*, p. 86. ‡ *Journ. Soc. Dyers and Col.*, 1906.

§ *Mon. Scient.*, Quesneville, 1894, p. 333. ‖ *Journ. Soc. Dyers and Col.*, 1897, p. 43.

¶ *Färber Ztg.*, 1894-95, pp. 226 and 328.

containing ¾ litre hydrochloric acid, 32° Tw., in 100 litres water, after which it is either allowed to drain well, or is hydro-extracted. It is then treated cold for 15 to 30 minutes in a clear solution of 1½ kilos. bleaching powder in 100 litres water, drained, soured in hydrochloric acid for 30 to 45 minutes, rinsed and turned for 15 to 30 minutes in a bath heated to 75° C., and containing 600 grms. Marseilles soap to 100 litres water, hydro-extracted, soured again in hydrochloric acid, as above, and then well washed. The yarn is apt to turn yellow by this process, but this may be prevented to some extent by adding the bleaching powder solution slowly. The colour is also improved by stoving, either before or after the treatment with soap, or by steeping the yarn for half an hour in bisulphite of soda, 64° Tw., diluted with three times its volume of water, and then souring. According to Clad & Co.* the yellow colour may also be removed by treating the wool in a warm bath of stannous chloride and hydrochloric acid.

If the wool is subsequently to be dyed in dark colours a larger proportion of bleaching powder can be taken. The souring is done at 70° C., and the yarn is then turned in the bleaching powder (10 to 20 per cent. of the weight of the yarn) for three-quarters of an hour.

According to Meister, Lucius and Brüning † better and more reliable results are obtained by treating the moist wool with gaseous chlorine.

To restore to chlorinated wool the natural feel, &c., of untreated wool, Florin and Lagache ‡ subject the treated material to the action of various salts, notably aluminium, zinc, tin, iron, and chromium salts of organic acids.

For the chlorination of piece goods the treatment is similar to that used for yarn, and the operation is best effected on a jigger, the bleaching powder solution being run in slowly.

Local chlorination of piece goods has been suggested by Knecht,§ with the object of producing crimp effects. The pieces are printed in stripes (not too narrow) with thickened sulphuric acid, passed through a weak bath of bleaching powder, rinsed, and milled in a soap solution. The chlorinated parts do not shrink under this treatment, and a permanent crimp is thus obtained. The process is only suited for light wool fabrics.

Behaviour towards Solutions of Metallic Salts.—Solutions of salts, which are neutral to litmus, such as sodium chloride, sodium sulphate, calcium chloride, &c., are quite without action on the wool fibre. Wool boiled in solutions of sodium chloride and calcium chloride absorbs only traces of these salts. But when boiled for some time in solutions of metallic salts, like aluminium sulphate, copperas, chrome alum, &c., which are acid to litmus, considerable quantities of the salt are taken up by the fibre. This takes place in the mordanting of wool, previous to dyeing it with adjective colours, and an exact knowledge of the chemical changes which take place would, therefore, be of considerable interest. It is a prevalent opinion that when wool is boiled with aluminium sulphate, for instance, the salt is decomposed by the fibre in such a manner that aluminium hydrate and sulphuric acid are formed, of which the former is assimilated by the fibre, while the latter remains in solution. Others again assume that an insoluble basic sulphate of alumina is formed on or in the fibre. Quantitative determinations, carried out by Fürstenhagen and Appleyard,‖ show that when wool is boiled with a solution of alum no free acid remains in solution when the amount of alum does not exceed 5 per cent. of the weight of the wool. When larger amounts are used a basic sulphate of alumina is fixed on the fibre.

Now it has already been shown that wool possesses a considerable affinity for both acids and bases, and, in its whole behaviour, it evinces the properties

* *Journ. Soc. Dyers and Col.*, 1896, p. 178. † *Ibid.*, 1898, p. 175.
‡ *Ibid.*, 1900, p. 109. § *Ibid.*, 1897, p. 21. ‖ *Ibid.*, 1888, p. 105.

of an amidoacid—that is, of a substance possessing simultaneously basic and acid properties. This would explain in a satisfactory manner the fixation of both the acid and basic constituents of the alum, but in what form these are fixed still remains a matter of conjecture. It is not improbable that the phenomenon is due to actual chemical combination with the fibre or with certain constituents of the latter; just as lead or mercury, when absorbed by the system, enters into chemical combination with the albuminoids in the various organs. That a hydrate is not formed is conclusively shown in mordanting wool with copper salts. The fibre assumes a green colour, but copper hydrate when boiled is at once dehydrated and transformed into black copper oxide. If copper hydrate had been formed, the fibre would be black, whereas it is green, and remains so even after prolonged boiling.

The behaviour of wool towards bichromate of potash in mordanting will be found under the heading "bichromates" among the mordants.

Cold solutions of *tannic acid* have little effect on the fibre, but when boiled in a solution of a tannin (like myrabolans, for instance) the wool appears to absorb tannic acid, and its properties become altered. If chromed wool is boiled in a decoction of logwood to which myrabolans have been added, it is said that it is impossible to dye it black. Messrs. Meister, Lucius & Brüning have patented a process for rendering wool incapable of absorbing dyestuffs,* which is apparently based upon this observation. The wool is boiled in a solution of tannic acid, and is then treated in a bath of tartar emetic.

Behaviour towards Colouring Matters.—Wool, of all textile fibres, exhibits the most powerful affinity for the colouring matters. It combines directly with all the substantive dyes, and can be readily dyed with them. Its affinity for these is generally greater than that of silk; in other words, the colours produced on wool resist the action of boiling water or of soap better than those on silk. Thus, if wool and silk are dyed the same shade with Naphthol yellow or Indigo extract and then boiled with water, the colour is extracted from the silk much more rapidly than it is from the wool. There are some exceptions to this rule, and on these facts is based the principle of dyeing the wool and silk, in mixed goods manufactured from these two fibres, two entirely different shades in one bath. As shown by Hirsch,† wool also evinces a strong affinity towards certain substances, like the naphthol sulphonic acids, which are not dyes in themselves, but are capable of forming dyes by subsequent treatment. Thus wool boiled in acid solution with 1 to 2 per cent. beta-naphthol disulphonic acid R, became orange when passed into a solution of diazotoluene after the addition of ammonia. In a similar manner Naphthol green may be produced on the fibre by boiling in naphthol monosulphonic acid, passing through an acidulated bath of nitrite of soda and then into a hot copperas solution.

For some adjective dyes, such as the insoluble red dyewoods and catechu, wool also exhibits a direct affinity. Others, like Alizarin, which are used in dyeing in the form of pastes containing the colouring matter in a very finely divided state, are absorbed mechanically and fixed loosely by the fibre.

The various qualities of wool behave differently in dyeing, the finer qualities generally requiring more dyestuff to produce a given shade than the coarser ones. The amount of dyestuff required also varies according as the wool is dyed as loose wool, slubbing, yarn, or in the piece; the former requires most, the latter least dyestuff.

Certain kinds of wool, like mohair, are sometimes very difficult to dye; they appear to take up only a very small proportion of the dyestuff, in spite of prolonged boiling. In these cases a short steaming is generally found to be effective in overcoming the difficulty. In some cases this peculiar action of steam on wool may be a drawback (see *Crabbing*, Part IV.).

* *Journ. Soc. Dyers and Col.*, 1901. p. 266. † *Ibid.*, 1889, p. 115.

Wool immersed in solutions of the diazo-compounds (*e.g.*, diazotised Paranitranilin) and then dried is dyed in shades varying from yellow to brown, which are very fast to washing. It was generally supposed that, in such cases, the wool combined with the diazo-compound to form an azodye, but Brandt* considers that no such action takes place, and that the colours are due to the formation of diazoamido-compounds.

SILK (Ger., *Seide;* Fr., *Soie*).

Silk is the fibrous substance which is excreted by the silkworm, and with which it envelopes itself in a *cocoon* when it enters into the chrysalis stage of its existence.

The numerous kinds of silk which come into commerce may be conveniently classed as *artificially* reared, and *wild* silks. The former are by far the most important. The principal species of silkworm is the *Bombyx mori*, or mulberry silkworm, which is reared in China, Japan, India, Italy, the South of France, Greece, and The Levant. The worms are reared in Asia in the open air, but in Europe this is done in specially constructed buildings or sheds, which the French call *magnaneries*. Here the eggs are laid out on shelves covered with white paper, and the temperature of the room is gradually raised during about twelve days from 18° to 25°. Under these conditions the eggs are hatched. The caterpillars are taken into a more spacious room, where they are fed on the leaves of the white mulberry (*Morus alba*). The caterpillars evince an enormous appetite, and grow rapidly to their maximum size in from thirty to thirty-three days, changing their skin every four to six days. At this stage their movements become slow, and they cease to take nourishment. They are allowed to creep into birch twigs, or bundles of broom or heather placed in their vicinity, where they spin themselves into cocoons.

Fig. 5.—Caterpillar, cocoon, and silk moth on mulberry twig.

The spinning lasts about three days, but in order to be sure that all the worms have finished spinning, five days are generally allowed to elapse before the cocoons are collected and killed.

The substance from which the fibre is produced is found in the silk worm before spinning in the form of a clear, colourless, sticky liquid, which is secreted from two glands situated symmetrically on either side of the body, and communicating with a capillary orifice in the head (the spinneret). According to Duseigneur, a section of the silk gland shows the presence of two liquids, an outer one, which in natural yellow silk is coloured yellow, and which constitutes from 20 to 25 per cent. of the whole, and an inner one

* *Journ. Soc. Dyers and Col.*, 1901, p. 177.

which is always colourless. These quantities correspond with the relative amounts of sericine and fibroine found in the raw silk.

On coming in contact with the air, the silk liquid solidifies, forming a uniform double fibre which in some places may be seen under the microscope separated into two fibres.

After the cocoons have been collected, and some of the finest sorted out for breeding, the rest are killed, either by exposing them in stoves to a temperature of 60° to 75° for three hours, or by steaming them for about ten minutes. In this state they are brought into the market.

The first mechanical operation to which the cocoons are subjected, after being sorted into different qualities, is that of *reeling*. The contrivances used for this purpose differ somewhat in their construction. The best results are produced, according to Wardle, by means of the Italian tavelette devised by Keller, and shown in Fig. 6.

It consists of an iron stand, A, 12 inches in height. B represents the cocoon and its thread, placed so as to show the position of the silk on the instrument. C is the *filière*, a porcelain disc, pierced in the centre and concave on the lower side. The threads of four or more cocoons pass through it and form a compound thread of "raw silk." At D is the *croissure* or crossing of the raw silk thread six or more times round itself. The object of this is to straighten and remove kinks and irregularities in the thread. E E are pulleys, the drums of which are formed of thin glass rods. F F are porcelain eyelets or guiders attached to a brass frame, which also supports the pulleys.

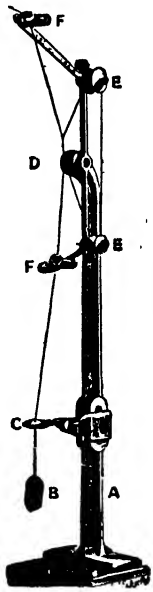


Fig. 6.—Keller's tavelette or silk reeling machine.

A number of cocoons are thrown into a basin, which contains water heated by gas or steam to about 60° C. The fibres of from 4 to 18 individual cocoons are collected by the operator and pass through the eye of the *filière*, thence following the same course, and ultimately through the guides, F, on to a reel. The operator always has a number of ends of fresh cocoons ready, so that as soon as one has come to an end, it is at once replaced by a fresh one. By the action of the hot water in the vessel, some of the gum or silk-glue becomes dissolved and causes the individual fibres to cohere and form one thread, which varies in thickness according to the number of cocoons constituting it.

A single fibre is known as *grège*. By combining a number of grège fibres and using additional twist, *organzine*, or warp silk, is produced, whilst by using a smaller number of fibres and adding less twist *trame*, or weft silk, is obtained.

The silk reeled direct from the cocoons is the most valuable quality, and constitutes the *raw silk* or *net silk* of commerce. The outer portions of the cocoon, which consist of a loose tangle of threads, are used in the manufacture of *floss silk;* the innermost layer which envelopes the chrysalis, also the pierced cocoons, double cocoons, and those which have been spoilt in steaming, constitute the inferior qualities, and are used for the manufacture of *spun silk*. For this purpose they are fermented with water, boiled with soda, washed and dried; after being torn to shreds, the material is combed, carded, and spun on machinery similar to that used for worsted. *Chappe silk* is produced in a similar manner, but without previously boiling the material.

Counts.—In thrown or net silk, the Manchester counts indicate the weight in drams per hank of 1,000 yards. For spun silk, the counts are the same as for cotton (*q.v.*).

In net silk, the counts are generally expressed in *deniers*. The weight of a denier is 0·0531 grm. and the standard of length of fibre taken is 476 metres. Thus, silk of 10 deniers would weigh 0·531 grm. for a length of 476 metres.

Structure of the Silk Fibre.—As it comes into the market raw silk appears in the form of a more or less coarse uniform fibre, generally of a light creamy white, but sometimes of a bright yellow colour (especially in Italian silk). It has a harsh feel and little lustre. As has already been pointed out, these fibres are made up from the individual fibres of from 4 to 18 cocoons. The fibre drawn from a single cocoon varies in length from 350 to 1,250 metres, and has an average diameter of about 0·018 mm. The diameter is greatest at the outside and diminishes towards the interior of the cocoon.

After removing the silk-gum, by boiling with soap, the silk separates into its individual fibres (Fr. *brins*), and is, in this condition, distinguished by its beautiful lustre, fineness, strength, and elasticity. Under the microscope it presents the appearance of a structureless, transparent, rod-shaped fibre. Under the influence of caustic soda these fibres are resolved into a large number of very fine filaments or fibrillæ.* This change often takes place unintentionally in the various processes to which silk is submitted, but chiefly in the boiling-off process, especially when carelessly conducted, and gives rise to "knots" (Fr. *flocons* or *pelotons*) in silk goods, which, under the microscope, present the appearance of bundles of very fine filaments. In dyeing, these knots attract colouring matter like the other portions of the fibre, but appear lighter in colour than the latter owing to their extreme fineness.

Physical Properties.—Silk has a specific gravity of 1·367. According to more recent determinations by L. Vignon, the raw fibre has a specific gravity of 1·33, and the boiled-off fibre of 1·34. It is a bad conductor of electricity, and easily becomes electrified by friction. This is a drawback to the manufacturer, but it can be overcome to a great extent by keeping the atmosphere of the room moist.

A silk fibre can be stretched one-seventh to one-fifth of its length without breaking. When treated with aqueous solutions of certain metallic salts, it may contract 0·7 per cent. in length. Raw silk possesses greater elasticity and greater tensile strength than "discharged" silk. By discharging the gum the strength decreases by 30 per cent., the elasticity by 45 per cent. When wetted, silk possesses less tensile strength, but greater elasticity than in the dry condition.

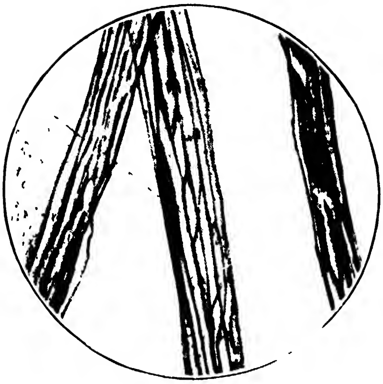
Like wool, silk is a very hygroscopic substance. It may be made to absorb up to 30 per cent. of its weight of moisture without feeling damp. This fact, coupled with the high price of silk, renders it necessary for the buyer on the one hand and the seller on the other to know exactly the "condition" of the silk in which a transaction is made. This is done in all the more important silk centres, like Lyons, St. Etienne, Paris, Crefeld, Milan, Zürich, London, &c., officially in the so-called conditioning houses.†

Up to the year 1841 the method employed for conditioning consisted in exposing the selected samples on trays for 24 hours to the air in a room heated to from 20° to 25° C., and ascertaining how much they lost or gained in weight. The method did not give satisfactory results, owing to the variations in the

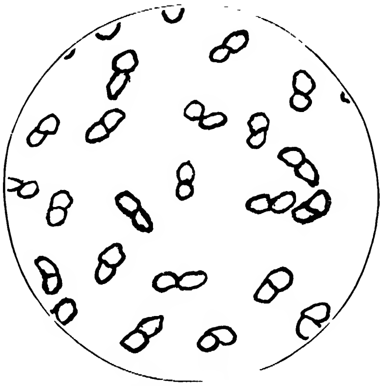
* A. and R. Sansone, *Journ. Soc. Chem. Ind.*, 1906, p. 1215.

† The first conditioning establishment for silk was founded in Turin in 1750 by order of the King of Sardinia. In 1779 one was founded in Lyons.

Plate V.

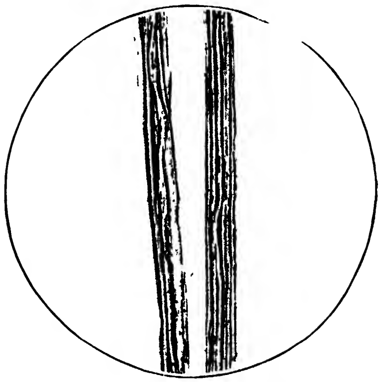


No. 25.—Raw silk. × 80 diam.

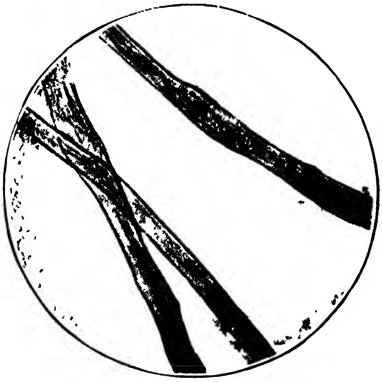


No. 26. Raw silk (section of fibre as reeled from cocoon). × 120 diam.

No. 27.—Individual silk fibres from boiled-off silk yarn. × 60 diam.



No. 28.—Raw silk. × 60 diam.



No. 29.—Tussur silk. × 60 diam.

No. 30.—Tussur silk (section). × 60 diam.

[*To face p.* 62.

hygrometric condition of the atmosphere. In 1841 Talabot introduced the method in use at the present time (with Persoz's improvement of drying in a current of air) of determining the absolute weight of the silk dried at 110° to 120° C. The whole bulk of the silk to be conditioned is weighed, and samples are taken out from various parts weighing in the aggregate about 1,500 grms. This sample is divided into three lots. Two of these are weighed to within 0·50 grm., and dried in a specially constructed apparatus in a current of air heated from 110° to 120° until the weight is constant. If the results are within a half per cent. of each other, the mean is taken; if not, the third lot is treated in a similar manner, and the mean of the three is taken. The condition of the bulk is then arrived at by adding to its absolute weight, which is calculated from the loss in weight of the samples, the legal quantity of moisture—viz., 11 per cent.

Chemical Composition and Properties of Silk.—Raw silk is not a uniform product, but consists of two substances—viz., the fibre proper (fibroïne) and the external covering, which is known as silk-gum or silk-glue (sericine). The silk-gum is soluble in boiling water or dilute soap solution, while the former is not. The silk-gum constitutes 20 to 25 per cent. by weight of the raw silk.

The silk fibre, freed from all impurities by treatment with water at 133° C., then with alcohol, and lastly with ether, constitutes what is chemically known as *fibroïne*. According to L. Vignon,* pure fibroïne can be obtained by boiling raw silk twice with soap, then extracting with hydrochloric acid, and then with alcohol of 90 per cent. Mulberry silk does not appear to vary much in its chemical composition, which corresponds to the formula $C_{15}H_{23}N_5O_6$. It exhibits the properties of an albuminoid (proteïd).

Prolonged boiling with water has a tendency to slightly weaken the fibre boiling temperatures are, therefore, avoided as much as possible in dyeing and discharging. Silk heated with water to 130° for three hours loses somewhat in tensile strength, whilst wool subjected to the same treatment is completely disintegrated.† Commercial "boiled-off" silk contains, on an average, 0·7 to 1 per cent. of ash, consisting principally of lime, magnesia, alumina, and iron.

Behaviour towards Acids.—Silk is rapidly attacked and dissolved by *concentrated* mineral acids. Concentrated hydrochloric acid is capable of dissolving more than its own weight of silk, a viscous, transparent mass resulting, from which alcohol throws down a copious precipitate. When diluted with water and neutralised, a flocculent precipitate is formed from this solution; it is soluble in ammonia.

Fischer and Skita‡ found the solution of silk in strong hydrochloric acid to contain for every 100 parts of silk :—

10 parts *l*-tyrosine,	1 to 1½ parts *l*-leucine,
21 ,, *d*-alanine,	1 ,, 1½ ,, *l*-phenylalanine.
36 ,, glycocoll,	

In a further communication, Fischer and Abderhalden state that the decomposition products include 12 parts methyldiketopiperazine.

Gaseous hydrochloric acid destroys silk without liquefying it. Nitric acid dissolves silk in the cold, forming a yellow solution (probably xanthoproteic acid). When silk is immersed for one minute in nitric acid of 27° Tw., it acquires a yellow colour which is fairly fast to light, and quite fast to water (*mandarinage*). It is necessary, however, that in order to obtain the result,

* *Comptes rendus*, 1892, cxv., p. 613. † *Journ. Soc. Dyers and Col.*, 1891, p. 58.
‡ *Ibid.*, 1901, p. 261.

the nitric acid should contain lower oxides of nitrogen in solution. By the action of ammonia or other alkalies, the pale yellow colour is turned darker and brownish.

Silk absorbs acids from dilute aqueous solution like wool does, and retains them tenaciously. The lustre of the fibre is at the same time increased, and the silk acquires a peculiar feel, emitting when compressed in bulk a peculiar crackling sound (*scroop silk; Fr., craquant*). This property is frequently desired by the purchaser. In order to produce it, the silk is worked, after dyeing, for a short time in a dilute solution of acetic, tartaric, or sulphuric acid (*brightening; Fr., avivage*), and then dried without washing. Tartaric acid gives the best results, but it is the most expensive. The scroop feel produced by acetic acid disappears after a time, owing to the evaporation of the acid.

By the action of acids of moderate concentration, silk contracts (according to Dèpouily & Garnier's French patent) like cotton does in mercerising. Consequently, if piece goods consisting of cotton and silk or of wool and silk are printed with acids of suitable concentration, the silk contracts, while the other fibre does not, and a puckered or crape effect is the result. The extent of the contraction depends upon three factors — viz., concentration of the acid, temperature, and time—but since the fibre suffers by the action, these factors must of necessity be kept within certain limits. The following figures give the maxima in this respect:—Sulphuric acid, 75° to 80° Tw. at 15° to 37° C. for 5 to 15 minutes; hydrochloric acid, 26° to 29° Tw. at 5° to 35° C. for 1 to 15 minutes; nitric acid, 54° to 60° Tw. at 5° to 45° for ½ to 15 minutes; and orthophosphoric acid, 90° to 100° Tw. at 25° to 45° C. for 2 to 15 minutes.

According to Fürstennagen and Appleyard, silk treated for an hour in a solution containing 22·5 per cent. of tartaric acid (calculated on the weight of the silk) absorbed 2·5 per cent. Silk boiled for one hour in a solution containing 20 per cent. of sulphuric acid (calculated on the weight of the fibre) retained 1·5 per cent. According to Lidow, glacial acetic acid, as well as molten citric and oxalic acids at elevated temperatures, dissolves silk rapidly and completely.

Behaviour towards Alkalies.—At 0° caustic alkalies have little action on the silk fibre, even if used in a sufficient degree of concentration to mercerise cotton. Advantage is taken of this in the production of puckered effects in silk material containing cotton binding threads at regular intervals in the warp and weft. Hot solution of caustic alkalies, however, dissolve silk completely, though not so readily as they do wool. Numerous decomposition products are found in the solution, amongst which one especially — viz., *sericinic* acid — is of interest, as showing similar properties towards the colouring matters to those of the lanuginic acid obtained from wool. In very dilute aqueous solution the caustic alkalies have little injurious effect on the fibre, and have been employed for discharging.

Ammonia has little action, even when applied hot. Alkaline carbonates act like the caustic alkalies, but much less energetically.

Of the milder alkalies, the soaps may be specially mentioned as having little or no injurious effect on the silk fibre. They are used largely in ungumming or discharging, and in various processes of dyeing. *Borax* is similar in this respect. Prolonged action of *lime water* destroys the lustre of silk and renders the fibre brittle.

Behaviour towards Oxidising Agents.—*Bichromate of potash* turns silk yellow, and by prolonged boiling a light olive; it is not suitable as a mordant. A strong solution of *chromic acid* rapidly destroys and dissolves the fibre.

Permanganate of potash turns the fibre brown and, if used in excess, tenders it. A subsequent treatment with bisulphite of soda or sulphurous acids bleaches the fibre.

Chlorine and the *hypochlorites*, if used strong, attack the fibre and destroy it; but, if used in very dilute solution, they increase its affinity for certain colouring matters, but nothing like to the same extent as is the case with wool.

Behaviour towards Metallic Salts.—In its behaviour towards metallic salts, like those of tin, aluminium, and iron, silk resembles wool. If soaked in cold and not too dilute solutions of these salts, an absorption takes place, which is due, as generally supposed, to the formation of a metallic hydrate, or of an insoluble basic salt on and in the substance of the fibre.* Thus, if silk is steeped over night in a solution of basic ferric sulphate, wrung and washed, it assumes a yellow to yellow-brown colour, according to the strength of the solution employed. The phenomenon which plays a most important *rôle* in the mordanting and weighting of silk still requires a satisfactory explanation. It is a remarkable fact that silk which has been weighted with stannic chloride or ferric salts and not thoroughly washed out is completely rotted if exposed to light.

A concentrated solution of zinc chloride (140° Tw.) rapidly dissolves silk to a thick sticky liquid, which can be diluted with acidulated water without the formation of a precipitate. By subjecting this solution to dialysis, the acid and zinc chloride are removed, leaving behind an aqueous solution of silk, which, when evaporated, leaves a brittle glass-like substance insoluble in water. If the solution in zinc chloride is diluted with water alone and not with acidulated water, a flocculent precipicate is obtained, which can be freed from the chloride of zinc by washing. A solution of this precipitate in ammonia has been used for coating vegetable fibres with silk. Less concentrated solutions of zinc chloride have the effect of causing the silk fibre to shrink, and have been utilised for the production of crimp effects in mixed fabrics (Miss Graissot's patent). The fabric is steeped for one-half to three hours in zinc chloride solution of 32° to 76° Tw., suspended in a chamber heated to 25° to 30° C. until the desired effect is obtained, and then washed.

Elsner has suggested the use of a solution of basic zinc chloride for the estimation of silk in presence of wool and cotton. The solution is prepared by dissolving 1,000 grms. zinc chloride and 40 grms. zinc oxide in 850 c.c. water, and should show a density of 144° Tw. in the cold. The weighed sample of the fabric is plunged into the boiling solution three times in succession, but should not remain immersed for more than one minute altogether. It is then freed from zinc by extraction with a 1 per cent. solution of hydrochloric acid. F. W. Richardson† contends that the solution also attacks wool and cotton, the former losing 1·5 to 2 per cent., and the latter 0·45 to 0·60 per cent. by the treatment.

Silk is soluble in Schweizer's reagent (solution of copper hydrate in ammonia), and also in a solution of nickel hydrate in ammonia. A solution prepared by dissolving 16 grms. copper sulphate in 140 to 160 c.c. of water, then adding 8 to 10 grms. glycerin and, subsequently, caustic soda solution until the precipitate which forms just redissolves, dissolves silk readily without affecting wool or cotton.‡

Better results are obtained, according to F. W. Richardson, § by means of an ammoniacal nickel solution.

* See also P. Heermann, *Journ. Soc. Dyers and Col.*, 1903, pp. 140 and 276; 1904, p. 13; 1906, pp. 166, 225, 282, 311, 312, and 313.

† *Journ. Soc. Chem. Ind.*, 1893, p. 429.

‡ Löwe, *Jahresberichte*, 1876.

§ *Journ. Soc. Chem. Ind.*, 1893, p. 424.

Tannic acid and *sugar* are also absorbed by silk, and are used in weighting.

Behaviour towards Colouring Matters.—In its behaviour towards the colouring matters silk resembles wool; but the affinity is, generally speaking, less. This applies especially to the acid colours which, when dyed on silk, are not as fast to water as on wool. Many colours do not dye as well at the boil as at about 60° C. Diazo-compounds unite chemically with fibroïne, presumably with the formation of azo-compounds. Thus silk treated with diazotised paranitraniline is dyed a beautiful (and fast) shade of "old gold."

According to Decker and Junkers, it is possible to deprive silk of its property of dyeing by alternate treatment with stannous acetate and soda.

For very delicate silk fabrics which would suffer by contact with water, the process of "dry-dyeing" is sometimes employed, which consists in dyeing the fabric in benzene solutions of suitable dyestuffs (fatty acid compounds or resinates of basic colours).

Silk-gum or *silk-glue*, the substance which envelopes* the silk fibre proper in its raw state, consists chemically of a substance called *sericine*, which in its composition is closely allied to fibroïne. The chemical formula ascribed to purified sericine is $C_{15}H_{25}N_5O_8$. It forms a transparent, glue-like mass, which swells up and dissolves in hot water. Water containing as little as 1 per cent. of sericine gelatinises on cooling; prolonged boiling, or the addition of small quantities of nitric or acetic acid or caustic potash, prevents the gelatinising. Sericine is precipitated from its aqueous solution by alcohol, tannin, and the salts of most of the heavy metals. When boiled with dilute sulphuric acid or with barium hydrate, sericine is decomposed, yielding products similar to those formed from fibroïne. Ris-Kummer † has patented a process by which the sericine can be rendered insoluble on the fibre by steeping the raw silk for three hours in a solution containing $\frac{1}{4}$ to $\frac{1}{2}$ per cent. formaldehyde. It is claimed that silk thus treated can be dyed hot without fear of any loss in weight.

The similarity in the composition of fibroïne and sericine has led to the supposition that the sericine is formed at the expense of the fibroïne as it leaves the spinneret of the silkworm by the absorption of oxygen and water, thus—

$$\underset{\text{Fibroïne.}}{C_{15}H_{23}N_5O_6} + O + H_2O = \underset{\text{Sericine.}}{C_{15}H_{25}N_5O_8}.$$

This theory is partly confirmed by the fact that if moist fibroïne is exposed for some time to the air, it becomes partially soluble in boiling water. Besides, the silk reservoirs contained in the worm are found to contain almost pure fibroïne, and very little matter soluble in water.

The sericine of raw silk contains, as a rule, small quantities of waxy, fatty, and resinous matters, and in the case of yellow silk, a natural yellow colouring matter. Dubois ‡ contends that the colouring matter of yellow silk is not a uniform substance, but contains:—

(1) A golden-yellow colouring principle, soluble in solutions of potassium carbonate, from which it is precipitated by excess of acetic acid in brilliant flakes. (2) Various crystals of a yellow colour. (3) A lemon-yellow amorphous colouring matter. (4) Lemon-yellow octahedral crystals, similar to those of sulphur. (5) A dark bluish-green pigment, in very small quantities.

* M. Moyret (*Mon. de la Teinture*, 1891, p. 324) asserts that the sericine obtained by the action of various solvents on raw silk does not exist as such on this fibre, but consists of products which have become chemically altered in the process of ungumming, just as glue does not exist as such in the substances from which it is prepared (hide bones, &c.).

† *Journ. Soc. Dyers and Col.*, 1896, p. 7. ‡ *Ibid.*, 1890, p. 171.

The same authority expresses the opinion that the yellow colouring matter of silk is analogous to, if not identical with, carotine.

When silk is boiled with hydrochloric acid, the sericine swells very much, without passing into solution, and ultimately remains as a hollow crumpled tube. In cold hydrochloric acid it also swells considerably, a property which is employed by v. Hohnel for the detection of the sericine envelope.

Towards alkalies, sericine is much more sensitive than fibroïne, boiling soap being sufficient to dissolve it all from the raw fibre, a treatment (known as discharging or "boiling-off") which is more particularly referred to in Chapter iv. The liquor thus obtained is technically known as "boiled-off liquor" (Germ., *Bastseife*), and is used by the dyer as an addition to the dye-bath, with the object of causing the colours to dye level. The levelling properties of boiled-off liquor are partly due to the presence of mucilaginous albuminous matter, and partly to the fatty acids which it contains. It is probable that the colouring matter, before combining with the fibre, forms loose compounds with these substances, which are slowly decomposed during the process of dyeing, the colour forming a less soluble compound with the fibroïne. For many colours it is necessary to acidulate the bath containing the boiled-off liquor. A milky liquid results, which contains the fatty acids in an extremely fine state of division, and not in lumps, as would be the case in the absence of dissolved sericine.

Since boiled-off liquor soon putrefies, it cannot be kept long; on the other hand, the silk dyer frequently runs short of his supply for other reasons. Consequently, in works principally engaged in colour dyeing, it is frequently desired to have a substitute. The following two recipes for this purpose may be mentioned:—

Two kilos. Marseilles soap, 200 grms. gelatine, and 100 grms. common salt in 100 litres condensed water.

One kilo. Marseilles soap is dissolved in 40 litres boiling water, and 250 to 300 grms. glue are separately dissolved in 10 litres boiling water. The two solutions are mixed and boiled. 130 to 150 c.c. olive oil are then added slowly while agitating, and the boiling is continued for a short time.

WILD SILKS.

Of the so-called wild silks that known as *Tussur* (Tussah or Tasar) is the most important. It is imported into this country from India and China; and, although formerly comparatively little known, is now used in large quantities.

The Indian Tussur is the product of the *Antheræa mylitta*, while the Chinese Tussur is the fibre of another species of the same genus—viz., *Antheræa pernyi*—both belonging to the family *Saturnidæ*. They do not appear to differ essentially from each other either in their physical or chemical properties.

Tussur silk comes into the market in the reeled state, and also in considerable quantities as spun silk. It always has a brown colour, which is difficult to remove. Tussur silk is much stiffer than ordinary silk, and, principally on this account, is more suitable than the latter for the manufacture of long-pile fabrics. The diameter of the fibres is also considerably greater; while mulberry silk has an average diameter of 0·018 mm., the fibre of Tussur silk averages 0·052 mm. The raw Tussur appears under the microscope to consist of a flat double fibre. Each of these individual fibres can be split up by suitable treatment into six to eight fibrillæ.

When seen in those parts where a twist in the fibre is prominent, it looks not unlike a cotton fibre, although differing from it in the high lustre and

greater transparency. The surface marking of the fibres consists principally of grooved lines, like the flutings of a column, and are evidently the result of the rising above the general surface of the fibre (before consolidation of the gum) of the small fibrillæ, of which every strand of the fibre is composed. The ribbon-like structure of the fibre gives it a peculiar appearance of unevenness in diameter, which thus appears to vary from $\frac{1}{500}$ to $\frac{1}{5000}$ of an inch.

Raw Tussur silk contains, as a rule, a high percentage of ash. In a sample of reeled Tussur (probably Chinese) Bastow and Appleyard * found 5·34 per cent. of ash calculated on the weight of the fibre dried at 100°. A quantitative analysis of the ash showed it to consist of—

Soda (Na_2O),	12·45	per cent.
Potash (K_2O),	31·68	,,
Alumina (Al_2O_3),	1·46	,,
Lime (CaO),	13·32	,,
Magnesia (MgO),	2·56	,,
Phosphoric acid (P_2O_5),	6·90	,,
Carbonic acid (CO_2),	11·14	,,
Silica (SiO_2),	9·79	,,
Hydrochloric acid (HCl),	2·89	,,
Sulphuric acid (SO_3),	8 16	,,
	100·35	,,
Oxygen equivalent to Cl,	0·65	,,
Total,	99·70	,,

The average of two ultimate analyses of the fibre, freed from all impurities, showed that it differs from ordinary silk in its chemical composition, as will be seen from the following table:—

	Tussur Fibroïne.	Mulberry Silk Fibroine.	
		Calculated for $C_{15}H_{23}N_5O_6$ (Cramer's Formula).	Calculated for $C_{71}H_{107}N_{24}O_{25}$ (Schützenberger's Formula).
	Per Cent.	Per Cent.	Per Cent.
Carbon,	47·18	48·78	50·26
Hydrogen,	6·30	6·23	6·31
Nitrogen,	16·85	18·97	19·84
Oxygen,	29·67	26·03	23·59
	100·00	100·00	100·00

F. Filsinger † has also estimated the amounts of nitrogen in mulberry silk and in Tussur silk by Kjeldahl's process. His averages work out on the dry fibre to 15·8 per cent. for Tussur and 17·7 per cent. for mulberry silk.

It contains, therefore, less carbon, about the same amount of hydrogen, considerably less nitrogen, and more oxygen than ordinary silk. This difference in the chemical composition is no doubt sufficient to account for the difference in the behaviour of the two fibres towards chemical reagents.

Behaviour towards Alkalies.—A considerable difference exists between the behaviour towards caustic soda of Tussur silk and ordinary silk; whereas the latter is soon dissolved in a boiling 10 per cent. solution of this reagent, Tussur silk requires a considerable time. A separation of the fibres may thus be effected. The same reaction may also be used for separating Tussur and wool in mixed fabrics or yarns.

* *Journ. Soc. Dyers and Col.*, 1888, p. 88.

† *Chem. Ztg.*, 1896, p. 324.

Behaviour towards Acids.—Ordinary silk dissolves in concentrated hydrochloric acid (sp. gr., 1·16) almost instantly, while Tussur silk only partially dissolves if left for even forty-eight hours in the cold acid.

A similar difference is manifested in the behaviour of the two fibres towards concentrated *zinc chloride* solution, in which ordinary silk is readily and completely soluble, while Tussur silk is dissolved only after a considerable time, and then not completely. *Chromic acid* dissolves ordinary silk at once, while Tussur is only acted upon slowly.

Bastow and Appleyard found in a sample of reeled Tussur—

Aqueous extract, ...	21·33 per cent.
Alcoholic ,, ...	0·91 ,,
Ethereal ,, ...	0·08 ,,

By boiling in distilled water and afterwards in soap solution, a total loss in weight of 26·49 per cent. was obtained. Sir Thomas Wardle* gives the following figures:—

Species of Silk.	Loss after Washing in Water at 46° C.	Loss after Boiling in Soap Solution.
	Per Cent.	Per Cent.
China Tussur, ...	13·7	21
Indian Tussur, ...	9	11
China silk, ...	2½	27
Japan silk, ...	8	30
Italian silk, ...	4	28
Bengal silk, ...	6⅔	30

Tussur silk possesses, even after successive treatments with alkalies and acids, a light yellowish-brown colour which is difficult to remove. It is more difficult to dye than ordinary silk, and this is accounted for, according to Wardle, by the different degree of solubility of the two silks. According to the same authority, the reason that the dyeing of black on Tussur silk is difficult arises from two causes—the first being the well-nigh impervious nature of the fibrillæ and their consequent impenetrability to the absorption of ordinary tinctorial and chemical agencies; and, secondly, the flatness of the fibre, which causes the light to be reflected at different angles to that of the round fibre of ordinary silk. This difference of structure causes the natural brilliancy of Tussur silk to be seen in scintillations instead of evenly diffused over the surface, and the silk, hovever well dyed, has a speckled, shiny appearance.

Of other wild silks, the following may be mentioned:—

Eria silk, the product of the *Attacus ricini*, which is found in various parts of India. What silk is produced from this source is almost entirely consumed in the native industries. It resembles Tussur silk.

Muga silk is the product of the *Antheræa Assama*, and is a native of Assam. The fibre is either white or of a light brown colour. and is easier to dye than Tussur silk.

Yamamai silk, the product of the *Antheræa yamamai*, is indigenous to Japan. In its microscopical appearance it is scarcely distinguishable from ordinary silk, except by the greater diameter of the fibre, which averages about 0·027 mm.

Sea silk or Byssus is the product of certain molluscs, principally *Pinna nobilis* and *Pinna rudis*, which inhabit the Mediterranean, and which are collected principally on the shores of Sardinia and Corsica. The fibres, which are excreted by these molluscs for the purpose of attaching themselves to the

* *Journ. Soc. Arts*, June, 1891

rocks, are of a golden brown colour, very soft, elastic, durable, and glossy. The diameter of the fibre varies from 0·013 to 0·055 mm. It differs from ordinary silk in being insoluble in acids and alkalies.[*]

ARTIFICIAL FIBRES.

Metallic Fibres or threads have been used for the manufacture and ornamentation of fabrics from very early times, but, since such fibres are never dyed (some are coloured by means of lacquers or by heating to elevated temperatures before coming into the hands of the manufacturer) or bleached, they do not directly interest the dyer. Metallic threads of Dutch metal are sometimes woven into grey cotton pieces which have to be bleached in the piece, and very careful treatment on the part of the bleacher is necessary, especially in the treatment with bleaching powder, in order to prevent these fibres being damaged.

Spun Glass, or glass wool, is a fibre possessing a beautiful silk-like lustre, obtained by the rapid and continuous drawing of molten glass into an extremely thin and flexible rod. It has not hitherto been successfully applied in the manufacture of fabrics, mainly on account of the brittleness of the fibres. Glass wool is naturally a very resistant substance, and finds some application in the laboratory for filtering strong acids or caustic alkalies. It cannot be bleached or dyed.

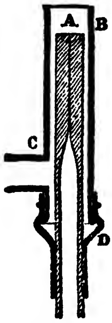


Fig. 7. Artificial silk spinneret.

Artificial Silk.—Within the past twenty years artificial fibres have been successfully prepared from solutions of nitrocellulose, cellulose, and gelatine, and some of these are at present manufactured in such a degree of fineness that, to the naked eye, they are indistinguishable from the best qualities of boiled-off silk. In a paper on the subject recently read by W. P. Dreaper,[†] it was stated that the output of artificial silk has now reached almost 8 tons per day.

If a solution of tetranitrated cellulose in a mixture of alcohol and ether be forced through a very small orifice into water, it instantly solidifies, and a continuous fibre can be drawn from the orifice which in its external appearance resembles silk. M. de Chardonnet, who was the first to make use of this interesting fact, has turned it to practical account for the manufacture of so-called *Artificial Silk*, which was practically demonstrated on the small scale at the Paris Exhibition of 1889. The pyroxylin employed is a tetranitrocellulose, which is first dissolved in a mixture of 38 parts ether and 42 parts alcohol so as to form a 6·5 per cent. solution. This latter is introduced into a small tinned copper vessel, from which it is forced by means of a continuous air pressure through a vertical glass tube (C, Fig. 7), ending in a fine capillary orifice (A), and surrounded by another glass tube (B), through which there is a continuous flow of fresh water. As soon as the pyroxylin solution comes in contact with water it solidifies, and may be reeled off in the form of a continuous fibre. Instead of one, two or more glass orifices may be fed from the same copper vessel; and the threads may either be reeled separately, or may be combined and reeled together. By the addition of certain colouring matters (*e.g.*, Safranine) to the collodion solution, uniformly coloured threads can be obtained. In consequence of the highly inflammable nature of pyroxylin, it is necessary to denitrate the product. This is effected

[*] Witt, *Chem. Techn. d. Gespinnstfasern*, p. 77.
[†] *Journ. Soc. Dyers and Col* 1907, p. 5.

by steeping in a solution of ammonium sulphide. The fibre is afterwards bleached in bleaching powder. Artificial silk has, according to M. de Chardonnet,* a specific gravity of about 1·49, and will bear a tensile strain of 25 to 35 kilos. per square millimetre of sectional area. The diameter may vary from 0·001 to 0·040 mm. The brilliancy or gloss of the fibre surpasses that of ordinary boiled-off silk.

In Pauly's process, mercerised cellulose is dissolved in Schweizer's reagent, so as to form a solution of sufficient consistency, and from this the fibre is drawn through an acid, which causes it to set immediately and at the same time removes the copper. This process, which is said to be considerably more economical than the Chardonnet process, is extensively used on the Continent, and yields a beautiful product known in Germany under the name "Glanzstoff," and in France as "Fils brillant."

In Stearn's process, a solution of viscose of suitable consistency is forced by pressure through a tube ending in a small platinum disc having five to eight very small holes. The threads are drawn off through a solution of ammonium chloride, which instantly precipitates the cellulose and thus solidifies the filaments. In appearance, the product is very similar to that obtained by the two preceding processes.

Numerous other processes for making artificial fibres from cellulose have been brought forward and patented,† but have hitherto met with but little success, practically all the artificial silk that comes into the market being made by one or other of the above processes.

The properties of the artificial silks vary somewhat, according to their mode of manufacture, but in some respects they show similar properties. Thus, they all possess very considerably less tensile strength than ordinary silk, and their elasticity is also less. They have a higher specific gravity, so that their covering power is not as great as that of ordinary silk; in other words, a given weight of artificial silk will not go as far as the same weight of real silk. Furthermore, they show the disadvantageous property of losing much of their tensile strength when in the wet condition, though they become strong again on drying. It is remarkable that cotton and linen, which also consist of cellulose, behave in exactly the opposite manner.

Chardonnet silk differs in its properties a good deal from the other two forms. It contains a small amount of nitric acid in combination, and would also appear to contain sulphur in the combined state, since, after prolonged extraction with pure bisulphide of carbon, it was found to contain 1·2 per cent. of sulphur. It dissolves more or less completely in caustic soda, and is thrown down again from the solution by the addition of acids as a gelatinous precipitate. Furthermore, it shows a direct affinity for the basic colours, with which it can be dyed without previous mordanting. The amount of nitric acid present in combination is not sufficient to account for this property, so that its affinity for basic colours is either due to the presence of oxycellulose or to that of the combined sulphur (thiocellulose?).

The two other kinds of artificial silk resemble ordinary cellulose in their chemical behaviour.

To distinguish between any of these artificial silks and ordinary silk, nitric acid or one of the acid colours may serve. These colour the ordinary silk, but leave the artificial fibres intact. A solution of 10 grms. copper sulphate and 5 grms. glycerine in 100 c.c. water, to which caustic soda has been added until

* *Comptes rendus*, cviii., p. 962.

† For further information on the subject, see Carl Süvern, *Die Künstliche Seide*, Julius Springer, Berlin, 1906. Also Bronnert, *Journ. Soc. Dyers and Col.*, 1900, p. 268; Bernard, *ibid.*, 1905, pp. 166, 190, 215; Sorlee, *ibid.*, 1906, p. 33; W. Massot, *Färber Ztg.*, 1907, pp. 146, 166, 201; and the current patent literature.

the precipitate which forms at first has redissolved, has no action on artificial silk, but readily dissolves real silk.

Numerous attempts have also been made to obtain artificial fibres from animal (albuminoid) substances, but none have hitherto been successful. A. Millar produced a fibre of beautiful appearance (Vanduara silk) by drawing a solution of gelatine to a fine filament, and then exposing this to an atmosphere containing formaldehyde, with the object of rendering the gelatine insoluble. The product has, however, not been satisfactory up to the present, partly on account of its want of tensile strength, but more particularly because, when wetted, it practically resolves itself into a jelly.

PART III.

WATER.

THE quality of water used for washing, scouring, bleaching, and dyeing purposes is a matter of the greatest importance. The use of an unsuitable water in such operations has, in innumerable cases, resulted in faulty work. Goods are frequently damaged to a greater or less extent from no other cause, and yet, in many instances, because the water happens to be bright and clear, it is never or rarely suspected of causing the mischief. Just as many people imagine that well water, if bright and clear and sparkling, must of necessity be of good quality for drinking purposes. It is known, however, that water may possess all these qualities and yet be little better than filtered sewage. Absolutely pure water never occurs in nature; even ordinary distilled water is not free from traces of other substances. For practical purposes, howevei distilled water may be taken as *pure* in considering the properties of water.

Pure water is a transparent, tasteless, inodorous liquid; colourless when seen in thin layers, but when a considerable depth is looked through, it appears of a pale greenish-blue to a deep blue tint. Under ordinary barometric pressure, water boils at the sea level at 100° C. and freezes at 0° C., the scale of the centigrade thermometer being constructed upon the melting point of ice and the boiling point of water. According to the thermometer which is commonly used in England (Fahrenheit's) the boiling point of water is 212° and the freezing point 32°. Since the boiling point of a liquid is dependent upon the pressure exerted upon its surface, the temperature of the water in a steam boiler is higher than 100° C. in proportion to the pressure of steam therein. With a pressure of 50 lbs. to the square inch, for example, the temperature of the water is 138° C. Water containing matter in solution boils under the ordinary pressure at a higher temperature than pure water. A saturated solution of common salt boils at 109° C., whilst a saturated solution of calcium chloride boils at 180° C. The amount of substances used in dyeing operations is, as a rule, too small to have any practical effect upon the boiling point of the solution. Where dye-vessels are heated by open steam pipes, the liquid may appear to be in violent ebullition and still have a temperature of several degrees below 100° C. Water, when heated from 0° to 4° C. contracts in volume, thus forming a striking exception to the almost universal law that bodies expand on heating and contract on cooling. When heated above 4° C. water gradually expands in volume until it reaches 100° C. and passes off as steam. At 4° C., therefore, water attains its maximum density. In other words, a given volume of water at 4° C. weighs more than at any other temperature. 10,000 volumes of water measured at 4° C. become rather more than 10,001 volumes at 0° C., and about 10,440 at 100° C. When water freezes it undergoes a sudden expansion, equal to about one-tenth of its volume. The force thus exerted is very great, the bursting of water pipes by frost being due to this cause.

AMOUNT OF SUBSTANCES DISSOLVED BY 1,000 PARTS OF WATER (GRMS. PER LITRE).

	Cold.	Boiling.
Potassium hydrate,	2,000	...
Sodium hydrate,	600	...
Calcium hydrate,	1·28	·79
Potassium chloride,	350	600
Sodium chloride,	360	404
Calcium chloride (anhy.),	2,000	...
Stannous chloride,	2,700	...
Potassium carbonate,	900	2,050
Sodium carbonate (anhy.),	160	490
Calcium carbonate,	·035	...
Potassium sulphate,	100	260
Sodium sulphate (anhy.),	150	425
Calcium sulphate,	2·3	2·1
Aluminium ammonium sulphate (common alum),	90	4,220
Ferrous sulphate (crys.),	36	320
Copper sulphate (crys.),	330	1,180
Potassium bichromate,	100	1,020
Sodium bichromate,	1,100	2,100
Potassium bitartrate,	4	105

Water is 815 times as heavy as air. One gallon weighs exactly 10 lbs. or 70,000 grains. The solvent properties of water are very great, greater in fact than those of any other liquid. The solubility of substances ranges from the merest trace to solutions containing much more solid matter than water. As a rule, the solubility of a substance increases with an increase of temperature. The exceptions, comparatively speaking, are very few; calcium hydrate and sulphate being, perhaps, the most familiar examples. Some salts, alum for example, are exceedingly soluble in boiling water, and only slightly soluble in cold. Others again, such as common salt, although freely soluble, are slightly more soluble at increased temperatures. The foregoing table shows the solubility of some familiar substances in cold and boiling water.

Water also possesses the property of dissolving gases. The colder the water the greater the volume of gas dissolved. The following table shows the solubility by volume of some gases in water at the ordinary temperature, 15° C.:—

	Volumes of gas dissolved by 1,000 volumes of water (c.c. per litre).
Nitrogen,	14·8
Hydrogen,	19
Oxygen,	29
Carbon dioxide,	1,002
Sulphuretted hydrogen,	3,233
Sulphur dioxide,	43 504
Hydrochloric acid,	462,000
Ammonia,	727,200

On account of the remarkable solvent power of water all natural waters contain more or less solid and gaseous matter in solution, varying greatly in quantity and in kind according to the nature of the strata with which the water has been in contact. For technical purposes we may conveniently classify natural waters into (1) *Rain water*; (2) *Spring and well water*; (3) *River and surface water*.

Rain water collected under suitable conditions is the purest form of natural water, but as it falls through the air it takes up various impurities present in

the atmosphere. Rain is, so to speak, water naturally distilled from the earth's great reservoir—the sea. That which is collected in the country is purer than that of towns. Rain water invariably contains carbonic, nitric, and nitrous acids; ammonia, oxygen, and nitrogen, and, usually, traces of saline matter as well as finely divided organic matter. The rain water of our large towns usually contains comparatively large quantities of sulphuric acid, derived from the combustion of sulphur in coal, in addition to small quantities of numerous other substances evolved from various manufacturing processes. After a long spell of dry mild weather the first shower of rain in such places is unusually rich in impurities. Rain water as actually collected, however, often contains many more impurities than those derived from the atmosphere, varying according to the nature of the roof upon which it has fallen. A slate roof gives the purest water. If collected upon lead or galvanised iron roofs small quantities of lead or zinc may usually be detected in the water. In many works, where only hard water is available, it would frequently be found advantageous to pay some attention to collecting and storing rain water, especially for scouring operations. One inch of rain on an acre is equivalent to rather more than 100 tons or 22,400 gallons of water. With an annual rainfall of 35 inches an acre of surface will thus yield on an average about 2,500 gallons of good soft water per working day.

Spring and Well Water.—Of the water which falls upon the earth as rain a portion evaporates, another portion runs off the surface forming brooks and rivers, and a third portion penetrates into the earth to a greater or less depth according to the nature of the strata. In some cases, after passing through a few yards of permeable strata, such as gravel, sand, or limestone, a less pervious stratum, such as clay, is reached where the water accumulates, and takes an underground course until the stratum crops out at the surface at a lower level. If a well be sunk along the course the water obtained therefrom is known as a *shallow well water*. On account of the comparative ease with which such waters can usually become contaminated by sewage and drainage from cultivated land, farm buildings, &c., they do not, as a rule, form desirable drinking waters, although they may be very good waters for dyeing and other purposes. In some cases the permeable strata do not crop out at the surface, but dip down under others which are impervious, or nearly so, when the water passes down to a great depth, and does not reappear at the surface unless it meets with a fissure and is forced upwards, forming a *spring;* or unless the overlying strata are bored through, so as to form an artificial spring or artesian well.

Spring and well waters usually contain considerable quantities of mineral matter derived from the rocks through which they have percolated. The salts most frequently found in such waters are carbonates, sulphates, chlorides, nitrates and silicates of calcium, magnesium, sodium, potassium, aluminium, and iron. Calcium and magnesium salts give to water the quality of "hardness," a term signifying the property which such waters possess of destroying the lathering properties of soap. Calcium and magnesium sulphates are soluble in pure water, but the carbonates (except in very small proportions) are only soluble in water containing carbonic acid. The rain, as it falls, contains a small quantity of carbonic acid; it acquires a further quantity from decaying vegetable matters in the soil, but a much greater amount from subterranean sources. When water is so highly charged with saline matter that it is unfit for either domestic or technical purposes it is commonly termed a mineral water, of which there are numerous kinds.

River water is principally composed of a mixture of rain, surface water, and spring water. It also frequently contains more or less drainage water from towns and villages, as well as numerous impurities from various works and

factories. River water contains, as a rule, much less dissolved matter than spring and well water, due principally to the admixture with surface water, which often contains very little matter in solution. A portion of the soluble matter in spring water is sometimes gradually deposited, owing to the disengagement of carbon dioxide. Carbonates of lime and magnesia and oxide of iron are thus frequently deposited in the beds of streams and rivers. Surface water from moorland districts is usually of a yellowish-brown or brown colour, due to the presence of peaty acids in solution and other forms of vegetable matter in suspension. River water usually contains a considerable quantity of suspended matter. The Thames contains from 15 to 30 grains per gallon, the Mississippi 56 grains, and the Ganges from 15 to 150 grains per gallon. In this way immense quantities of solid matter are carried into the sea. The Amazon contains only 2 grains of suspended matter per gallon, yet it discharges about 980,000,000 tons of mud into the sea every year.

For Technical purposes the matter in solution is of much more importance than that in suspension, since the latter may be removed with comparative facility by mere subsidence only or by filtration. The analysis of water is treated in another portion of this work (see under *Analysis*); but a few simple tests may be here given, which, if applied at the same time to a water whose composition and qualities are known, will frequently be found of service.

Calcium or lime salts are indicated by the formation of a fine white precipitate on the addition of a few drops of a solution of ammonium oxalate and ammonium chloride to the solution.

Magnesium Salts.—After adding ammonium oxalate in testing for lime, the liquid is boiled and filtered, and the clear filtrate evaporated to about one-tenth of its bulk. When nearly cold a little ammonia and sodium phosphate are added, which produce a crystalline precipitate in the presence of magnesia.

Sulphates, if present, will give a white precipitate on the addition of a few drops of hydrochloric acid and a little barium chloride.

Bicarbonates and free *carbonic acid* give a white precipitate on the addition of clear lime water.

Chlorides give a white curdy precipitate on the addition of nitric acid and silver nitrate.

Many natural waters, when evaporated down to a small bulk, become turbid. This may be due to the presence of either bicarbonates of lime and magnesia or sulphate of lime. If, on the addition of a few drops of hydrochloric acid, effervescence takes place, and the liquid becomes clear, carbonates only are present. If, on the other hand, no effervescence whatever occurs, and the liquid remains turbid, the deposit consists of calcium sulphate. The presence of both carbonates and sulphates is indicated by effervescence on the addition of hydrochloric acid, with but partial clearing of the liquid.

Waters containing salts of lime and magnesia give a white curdy precipitate when mixed with a solution of soap in weak alcohol, and no froth or lather is produced until sufficient soap has been added to combine with the whole of the lime and magnesia present.

Iron, if present in considerable quantities, will usually form a reddish-brown deposit when the water is freely exposed to the air for some hours. Smaller quantities may be detected by evaporating nearly to dryness with addition of hydrochloric acid and a drop or two of nitric acid. If potassium ferrocyanide be now added, a blue precipitate or greenish-blue colouration will be produced, according to the amount of iron produced. If potassium thiocyanate be added in place of ferrocyanide a red colouration will be obtained.

Alkaline carbonates may be detected by boiling the water for about ten

minutes, filtering and adding either litmus, lackmoid, or phenolphthaleïn. The first two indicators are turned blue, the last red.

Acid waters turn a neutral solution of lackmoid red.

Organic matter in quantity gives to the water a brownish colour, and, in some cases, rises to the surface as a brown scum (especially if a little alum is added) when the water is boiled. Water containing organic matter when evaporated to dryness leaves a residue of a yellowish or brownish colour, which on ignition becomes at first darker brown or black. On continuing the heat, the separated carbon burns away, and the residue then becomes white or grey, unless much iron is present, when it is brown.

Water for Boiler Purposes.—In a steam boiler, since practically pure water comes off as steam, the solid matter in solution gradually accumulates and, in most cases, a portion of it, sooner or later, is deposited. If the deposit is of a loose, powdery character, it forms what is known as "boiler mud;" if it becomes firmly attached to the boiler plates it is known as a boiler "incrustation." Waters which form a hard incrustation are either to be avoided for boiler purposes or they should be treated in such a manner as to prevent its formation. Incrustations not only cause much loss of heat, but the boiler plates are liable to be damaged through overheating. An incrustation is usually associated with a "hard" water, and there are many large users of steam who consider that incrustations are formed in proportion to the hardness of the water used. This is a mistake, since much depends upon the character of the salts constituting the hardness. A comparatively soft water may produce a hard scale much more quickly than a very hard one. If, for example, the hardness of a water was due entirely to either calcium chloride or magnesium sulphate (which is seldom the case, however), no incrustation would be formed under ordinary conditions, since both are very soluble salts. If the hardness of the water used is *entirely* due to bicarbonates, the excess of carbon dioxide is quickly given off in the boiler and carbonates of lime and magnesia are precipitated, not on the boiler plates, but as a loose powdery mass. If the hardness is due entirely to sulphate of lime, no precipitation takes place until the water becomes very much concentrated—until it contains about 150 * grains of calcium sulphate per gallon. At this stage, the water is saturated, and further concentration causes the calcium sulphate to crystallise on the boiler plates in the form of a hard deposit. When calcium and magnesium carbonates are present as well, these salts also become incorporated with the calcium sulphate. Water containing magnesium bicarbonate deposits at first magnesium carbonate; but Driffield, in a valuable paper on "Boiler Management," † has shown that boiler incrustations, though thrown down as a powdery mass, contain the magnesia in the form of hydrate, MgH_2O_2. He further points out that this hydrate of magnesia (even in the absence of calcium sulphate) is liable to bake into a hard scale if the flues are not well cooled down before the boiler is blown off. Calcium carbonate may also bake on to the plates under the same conditions, but not so readily as magnesium hydrate. In order to prevent the formation of scale in steam boilers, numerous so-called "boiler compositions" have been proposed and used. Some work satisfactorily, but the majority are altogether useless and, in some cases, positively injurious. A compound may, of course, act beneficially with one kind of water and yet be altogether useless for another. The best way is to remove the scale-forming ingredients, before the water enters the boiler, by one or other of the methods given under *Water Purification* (p. 80).

* This figure represents the solubility of calcium sulphate under the ordinary atmospheric pressure. Under increased pressures, however, calcium sulphate is almost insoluble in water.

† *Journ. Soc. Chem. Ind.*, 1887, p. 178.

Driffield shows, however, in the paper above mentioned that very satisfactory results may be obtained by merely adding sufficient sodium carbonate to convert the calcium sulphate into calcium carbonate. Water containing magnesium chloride is liable to act injuriously upon the boiler plates, from its decomposition into magnesium hydrate with evolution of hydrochloric acid. If magnesium chloride, therefore, be present, sodium carbonate should also be added in sufficient quantity to convert it into carbonate.

Water for Scouring, Washing, and Bleaching Purposes.—In all these operations salts of lime, magnesia, and iron are very objectionable. Iron is usually present in very much smaller quantities than lime and magnesia, but traces of iron in water are frequently the cause of much trouble. When soap is added to such waters no lather is at first produced, since the fatty acids of the soap combine with the lime and magnesia (as well as oxide of iron) to form sticky insoluble soaps possessing no detergent properties. No lather is produced until sufficient soap has been added to combine with the whole of the calcium and magnesium present. The soap is thus commonly said to be "killed." In this manner large quantities of soap are destroyed. One pound of calcium carbonate, or its equivalent in calcium sulphate or magnesium salts, dissolved in water precipitates, and, so far as its detergent qualities are concerned, destroys about 10 lbs. of good average soap. A water used for scouring yarn, submitted for analysis to one of the authors, was found to contain 35 grains of calcium and magnesium salts per gallon. Consequently, 1,000 gallons of this water (providing no free alkali were added as well) would destroy or render useless at least 50 lbs. of good soap. The "hardness" of a water is commonly expressed in degrees, but unfortunately some confusion exists regarding the exact meaning of the term. It may refer to parts of calcium carbonate (or equivalent in other salt) per 100,000, or to grains per gallon = parts per 70,000. Again, the hardness expressed in degrees may, or may not, include the hardness of pure distilled water. According to Wanklyn, distilled water has a hardness equal to 1 grain $CaCO_3$ per gallon. On Wanklyn's scale a water containing 9 grains of calcium carbonate per gallon possesses a hardness of 10°, whereas on Clark's scale (adopted by most chemists), or its equivalent in parts per 100,000, such a water would be 9° of hardness. Until comparatively recently, the hardness of a water was invariably determined by means of a standard solution of soap; but since other and more exact methods are now frequently employed (see under *Analysis*), it seems preferable to employ the term "degrees of hardness" as synonymous with either "parts $CaCO_3$ per 100,000," or "grains $CaCO_3$ per gallon." The latter form is employed in this work, unless otherwise stated. If the "soap test" were perfectly reliable and accurate, there might be some reason for allowing 1° for the *pure* water, but every chemist who has had any experience with waters knows that in many cases the "test" is most erratic. This has been clearly shown in a valuable paper on the "Examination of Water for Technical Purposes," by A. H. Allen, in the *Journal of the Society of Chem. Industry*, 1888, p. 795.

A thousand gallons of water for every degree of hardness destroys about 1 lb. 7 ozs. of soap, but this loss of soap is not by any means the only disadvantage. The sticky, insoluble calcium and magnesium soaps which are precipitated are liable to be deposited irregularly on the goods, and such being the case, uneven dyeing—especially with "mordant" colours—is almost invariably the result. If more than a trace of iron is present in the water, an insoluble iron soap will be precipitated on the fibre, and on being subsequently dyed with any "mordant" colour, the shade will be dull and probably stained. For bleaching purposes, water containing iron is very objectionable, whether the goods are to be subsequently dyed or to remain white. Very

small quantities of oxide of iron are sufficient to give a yellowish tinge to bleached fabrics, and to dull such shades as Turkey red. Water highly coloured with organic matter (peaty acids) is unsuitable for bleaching and stoving purposes.

Water obtained from the lower beds of the coal measures often contains large quantities (20 to 40 grains per gallon) of sodium carbonate. Such water, in the absence of earthy carbonates, acts beneficially in scouring operations, and is highly valued by wool-combers and manufacturers who use large quantities of soap.

Water for Mordanting and Dyeing Purposes.—The most troublesome waters to the dyer are those containing iron (in any form), and carbonates of lime, magnesia, and soda. Sulphates have little or no action in dyeing, but in the subsequent washing operations a considerable amount of earthy sulphates in the water may act injuriously in certain cases by "saddening" or dulling the colours. In mordanting operations, the carbonates produce precipitates with salts of iron, aluminium, tin, &c., and reduce bichromates to neutral chromates. The active ingredient is thus rendered much less effective as a mordant. If organic acids or acid salts (such as tartar) are used, a portion is neutralised and thereby rendered useless. Alkaline carbonates act more powerfully in these respects than calcium and magnesium carbonates. In dyeing operations, carbonates modify the colours produced with various dyes—especially cochineal scarlets, which are rendered much bluer than shades dyed in pure water. Many colouring matters, such as Methyl violet, Victoria blue, Coeruleïn, Alizarin blue, &c., are precipitated by carbonates. The dye thus works on to the material in a loose form and in many cases produces stains. It is not thoroughly fixed; and, when rubbed, much of the colour is removed, and stains whatever material it comes in contact with. The injurious effect of carbonates in water is strikingly illustrated in the dyeing of Alizarin blue and Coeruleïn. In some cases, as, for example, in the dyeing of Alizarin red (either upon wool or cotton), lime salts are decidedly beneficial when the material has been mordanted with aluminium compounds. The effect of acetate of lime in dyeing with Alizarin upon wool has been clearly illustrated by Hummel.* Alkaline carbonates retard the dyeing of many colouring matters; a small quantity of sodium carbonate, for example, is sufficient to prevent logwood working at all. Earthy carbonates in moderate quantity produce deeper, though duller, shades with logwood, fustic, &c. In dyeing with "acid" colours, neither sulphates nor carbonates have practically any effect. The amount of acid used, as a rule, is great in proportion to the alkalinity of the water. And, as large quantities of sodium sulphate are generally added at the same time, the comparatively small quantities of calcium, magnesium, and sodium sulphates (formed by the action of the sulphuric acid on the carbonates), cannot be expected to appreciably affect the results. In many cases, after the dyeing proper, the colour is seriously injured by washing or showering with water containing a large amount of earthy and alkaline carbonates. Too little importance is often given to the kind of water used in washing dyed goods. The effect of *iron* in water used for dyeing is to "sadden" or dull almost all "mordant" colours. A very small quantity, either in the mordant or dye-bath, has a most marked effect upon shades produced with such colouring matters as Alizarin red, cochineal, &c. The effect is much greater when separate baths are used for mordanting and dyeing than when the single-bath method is adopted. In the latter case the bath is usually of an acid character, and the iron does not readily work on to the fabric. With "acid" dyes, the amount of iron usually present in natural waters produces little or no effect.

Lead is seldom present in water used for dyeing, but its action in wool

* *Journ. Soc. Dyers and Col.*, 1884, p. 11.

dyeing has been studied by Rawson * (see p. 51), who finds that bright colours dyed in a neutral bath are very much affected, whereas in the presence of acids the same amount of lead has no action.

Correction of Water used in Dyeing.—Methods for the general purification of water are described below, but, in the absence of iron, for most dyeing purposes all that is necessary is to carefully neutralise the earthy and alkaline carbonates, which may be present, with an acid. This may be done in the mordant or dye-bath with either sulphuric, oxalic, or acetic acid. Sulphuric acid is much the cheapest, but great care must be taken not to use too much; otherwise bad results will be obtained. On this account, in dyeing with Alizarin blue, Coeruleïn, and other similar colours in calcareous waters, it is much better to use *acetic* acid, since a slight excess does no harm. In mordanting with bichromates, sulphuric acid may be used with advantage for neutralising any carbonates. The amount of sulphuric acid (D.O.V.) required for 1,000 gallons of the water may be readily ascertained in the following manner:—Pour 1 litre of the water into a white basin and add a few drops of a solution of methyl orange. Add from a burette, during constant stirring with a glass rod, a solution containing 6¼ grms. of the same sulphuric acid in a litre of distilled water until the colour of the liquid changes to red. The *number of cubic centimetres* thus required corresponds to the *number of ounces* of sulphuric acid to be added to 1,000 gallons of the water.

For direct cotton colours and sulphide colours it is best to boil the water with a little soda (about 3 ozs. soda ash per 1,000 gallons water for each degree of hardness), so as to convert both the bicarbonate and the sulphate into normal calcium carbonate.

PURIFICATION OF WATER.

The supply of water is frequently of such a quality that it is found desirable to effect some means of purification. On a small scale, for the laboratory, &c., water is best purified by distillation. In many works a considerable amount of distilled or condensed water is obtained from the steam pipes and used for scouring purposes. This practice might be much more widely adopted; the condensed water could not possibly be used to greater advantage. A pure soft water is a greater necessity in scouring than in any other operation.

Suspended matter in water is readily removed by filtration through beds of sand and gravel or engine ashes. Many other substances, especially iron, are wholly or partially removed by exposure to air in large shallow dams and subsequent filtration. Waters highly charged with bicarbonates give off a portion of their carbon dioxide, and normal carbonates are precipitated. Excepting waters containing ferrous carbonate, however, the change takes place very slowly and is never complete. Ferrous carbonate in water is quickly decomposed on exposure to air, and ferric hydrate is thrown down as a reddish-brown precipitate.

Several methods for the filtration of large quantities of water are described by A. Steiger in the *Journal of the Soc. of Dyers and Colourists* (1886, p. 185), as also in the *Journal of the Soc. of Chem. Industry* (1886, p. 416).

For the purification of water by chemical means numerous substances have been proposed. The principal impurities to be removed are bicarbonates and sulphates of lime and magnesia, as well as iron and organic matter. It has been already stated that bicarbonates in water are decomposed and precipitated by boiling A similar effect is produced by adding calcium or sodium hydrate to the water. When lime is used, the free carbonic acid unites with it to

* *Journ. Soc. Dyers and Col.*, 1889, p. 58.

form calcium carbonate, which is precipitated as well as the calcium or magnesium carbonate previously existing in the form of soluble bicarbonates. When caustic soda is used, sodium carbonate is formed, which remains in solution. The following equations illustrate the changes which occur:—

$$CaO(CO_2)_2 + Ca(HO)_2 = 2CaCO_3 + H_2O.$$
$$MgO(CO_2)_2 + Ca(HO)_2 = MgCO_3 + CaCO_3 + H_2O.$$
$$CaO(CO_2)_2 + 2NaHO = CaCO_3 + Na_2CO_3 + H_2O.$$
$$MgO(CO_2)_2 + 2NaHO = MgCO_3 + Na_2CO_3 + H_2O.$$

It is very important that the exact amount of precipitant should be added; otherwise, when lime is used, the water may be rendered harder than it previously was, either by a deficiency or an excess. If the water contains much free carbonic acid, a small amount of lime may be converted into bicarbonate and remain in solution. On the other hand, if too much lime is added, the whole of the carbonic acid is removed, but calcium hydrate remains in solution. The treatment with lime or soda also removes any iron which may be present in the water as well as a portion of the organic matter. When much organic matter is present, in order to obtain good results, it is necessary to employ some soluble salt of alumina or iron in addition to lime or soda. The alumina or ferric oxide formed carries down the organic matter, and also causes the carbonates of lime and magnesia to settle more rapidly.

Waters containing sulphates* of lime and magnesia undergo no change on boiling (unless highly concentrated), and are not acted upon by calcium hydrate.† Sodium hydrate acts differently according to whether sulphate of lime or sulphate of magnesia only is present, or whether carbonates are present as well. In the absence of carbonic acid, sodium hydrate produces no effect upon water containing calcium sulphate; but magnesium sulphate is precipitated as hydrate, in accordance with the following equation:—

$$MgSO_4 + 2NaHO = Mg(HO)_2 + Na_2SO_4.$$

When carbonic acid is present in water, either free or as bicarbonate, on the addition of sodium hydrate, sodium carbonate is formed, which then reacts upon calcium sulphate with the formation of carbonate:—

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

Unless calcium sulphate is present in excess, the addition of caustic soda thus effects the removal of both carbonates and sulphates of the alkaline earths.

If the free carbonic acid present is but small in amount, or the calcium sulphate excessive, an addition of sodium carbonate must be made. Sodium carbonate also precipitates magnesium salts as carbonate; but the hydrate of magnesia is less soluble than the carbonate, hence caustic soda is the best precipitant. The method of purification by means of lime is commonly attributed to the late Dr. Clark, of Aberdeen; although, according to the late Dr. Angus Smith, the use of lime was first proposed about a century ago by Thomas Henry, of Manchester. In its simplest form, as originally devised, two tanks or reservoirs are employed, one being used for mixing the hard water with the requisite amount of milk of lime or preferably clear lime water; and the other, to receive the purified water after the insoluble matter has been allowed to subside. A better plan is to have two mixing or precipitating vessels of such a size that each will hold sufficient water for a day's supply. The precipitated calcium and magnesium carbonates settle slowly,

* Nitrates and chlorides are acted upon in a similar manner to sulphates.

† Calcium hydrate added to water containing magnesium sulphate produces a precipitate of magnesium hydrate, but a corresponding amount of calcium sulphate remains in solution.

and the vessels used should, therefore, be shallow. On this account, a considerable space is required to carry out the process with success. Of late years, however, numerous machines have been devised with the object of economising space and time, as also of obtaining a continuous flow of pure soft water.

In the *Journal of the Society of Chemical Industry* (1884, p. 51), J. H. Porter describes an apparatus which is known as the **Porter-Clark** machine.

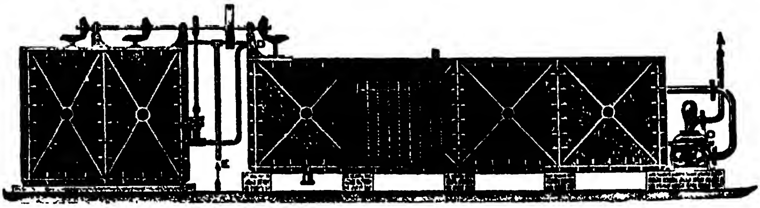


Fig. 8.—System of reservoir and tank filtration.

Since that was published, Messrs. Porter & Sons have introduced several modifications. One form, representing a "system of reservoir and tank filtration," is shown in Fig. 8.

The tank, A, on the left is used for dissolving the lime or other reagents necessary to soften the water. The longer tank, B, consists of mixing chamber and filtering compartment. In the latter, the series of pendent filtering mats and cloths have their perforated pipes connected by a main pipe. When the softened water has to be raised to a higher level, the main pipe is connected with a pump, C, as shown in the figure. The filtering mats are made of cocoanut fibre, and covered with closely-woven twilled cotton cloth. Each set may be readily raised and cleaned without necessarily stopping the progress of the operation. The water is supplied to the two tanks by the pipe, E. It flows into the mixing chamber along with a regulated quantity of the necessary reagents at the point, D.

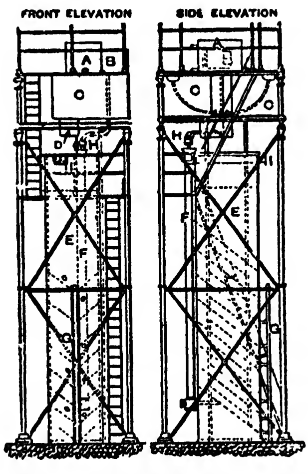


Fig. 9.—Stanhope purifier.

In a valuable paper entitled "Recent Improvements in the Treatment of Water for Technical Purposes,"* Macnab and Beckett describe an apparatus invented by Messrs. Gaillet & Huet, which is known in England as the **Stanhope Purifier**. In the majority of cases treatment with a mixture of lime and caustic soda is found most suitable, although, of course, other reagents may be used when required. The following description is taken from the above-named paper:—

In the annexed diagram (Fig. 9) the same letters refer to the same parts in both figures. A is a store tank containing caustic soda solution of 46° Tw. (sp. gr. 1·231); B is a tank receiving the water to be treated, which is maintained at a constant level by means of a valve and float. C and C are two tanks for use alternately, in which the lime water is prepared, a measured quantity of caustic soda being added at each time of charging, this mixture constituting the reagent. D is a small tank for maintaining a constant head of reagent. E is the clarification tank in which the

* *Journ. of the Soc. Chem. Industry*, 1885, p. 267.

decantation is accomplished, and which will presently be referred to in detail. F is a large pipe in which the mixture of water and reagent takes place. G is a pipe in connection with cocks for drawing off the sludge as it accumulates in the angular spaces in the clarification tank. At H are the pipes provided with graduated quadrants for conveniently adjusting the quantities of water and reagents. I is the delivery pipe for the softened water. The clarification tank, E, contains a number of thin diaphragms or shelves of a V shape, inclined at an angle of 45°, as shown by the dotted lines; these are rivetted alternately to the two opposite sides of the tank, and their position forces the water to take a serpentine course through the tank. A bed of wood shavings, contained between wire nettings, in the positions indicated by the two lines of rivets near the top, serves as a safety filter to stop any particles which have escaped subsidence. The water supplied to the apparatus at B is conveyed by a pipe to H, where it flows into the mixing pipe along with the reagent from C and D, the quantities being regulated by the cocks at H. The mixture of the water and reagent being effected by falling together into the funnel of the pipe, F, precipitation at once commences, and the whole, travelling down the pipe, enters the clarification tank by a branch pipe near the bottom, whence it rises in a serpentine course to the top, whilst the clear and softened water overflows into the delivery pipe at I. The precipitate on settling out finds its way down the inclined shelves to the angular spaces connected with the sludge cocks, by opening which the mud is removed without interrupting the process. The whole operation is thus a continuous one, and the labour involved consists in discharging the precipitate by opening the sludge cocks about once a day, and in the preparation of the reagent at long intervals. In place of the two lime tanks, a simple automatic apparatus is sometimes employed for preparing the lime continuously.

Archbutt and Deeley have described, in the *Journal of the Soc. Chem. Industry* (1891, p. 511), a method of purification, which, at a comparatively small cost, has given excellent results. Since that time, however, an improved method of mixing the water with the reagents has been introduced. The process is carried out in plain tanks, but owing to the rapid method used of mixing the reagents with the water, and the subsequent treatment which the mixture receives, the precipitate is caused to settle very quickly, and only comparatively small tanks are required. A special feature of the process consists in mixing the mud from the bottom of the tank obtained from previous operations with the water and the necessary reagents. This is found to have a remarkable effect in promoting the rapid subsidence of the precipitate.

The accompanying diagram (Fig. 10) shows the elevation and plan of a purifier capable of softening 10,000 gallons per hour. It consists of a cast-iron tank, divided into two equal parts by a transverse partition. The two tanks thus formed are fitted up exactly in the same way, the processes of filling, softening, and clarifying being carried on in one, whilst the softened and clarified water is being drawn off from the other.

Hard water is admitted to either tank by means of the supply pipe (1), which is connected up to a pump or main. The water is run up to the level of a gauge mark on the side of each tank. While the tank is filling quicklime and sodium carbonate, in proportions which depend upon the character of the water, are weighed out and boiled up with water in the small reagent tank (2). Some waters require also the addition of a little alumino-ferric sulphate, which is best added in solution direct to the tank immediately after the other ingredients have been run in. When the large tank is full, and the inlet valve has been closed, steam from the boiler is admitted to the blower (3), causing a current of water to circulate through the rose (4), the three-way cock (5), down the vertical pipe (6), and back into the tank through the perforations in the

upper row of horizontal pipes (6). On opening the small tap (7), the prepared solution is slowly drawn into the circulating current, and thus diffused throughout the body of water in the tank. The cock (8) is next opened to admit air through the pipe at the top of the blower, and by reversing the three-way cock (5) the air is forced through the perforations on the under side of the *lower* row of pipes (9). From these it rises in streams of bubbles, stirring up much of the precipitate produced in previous operations. In this

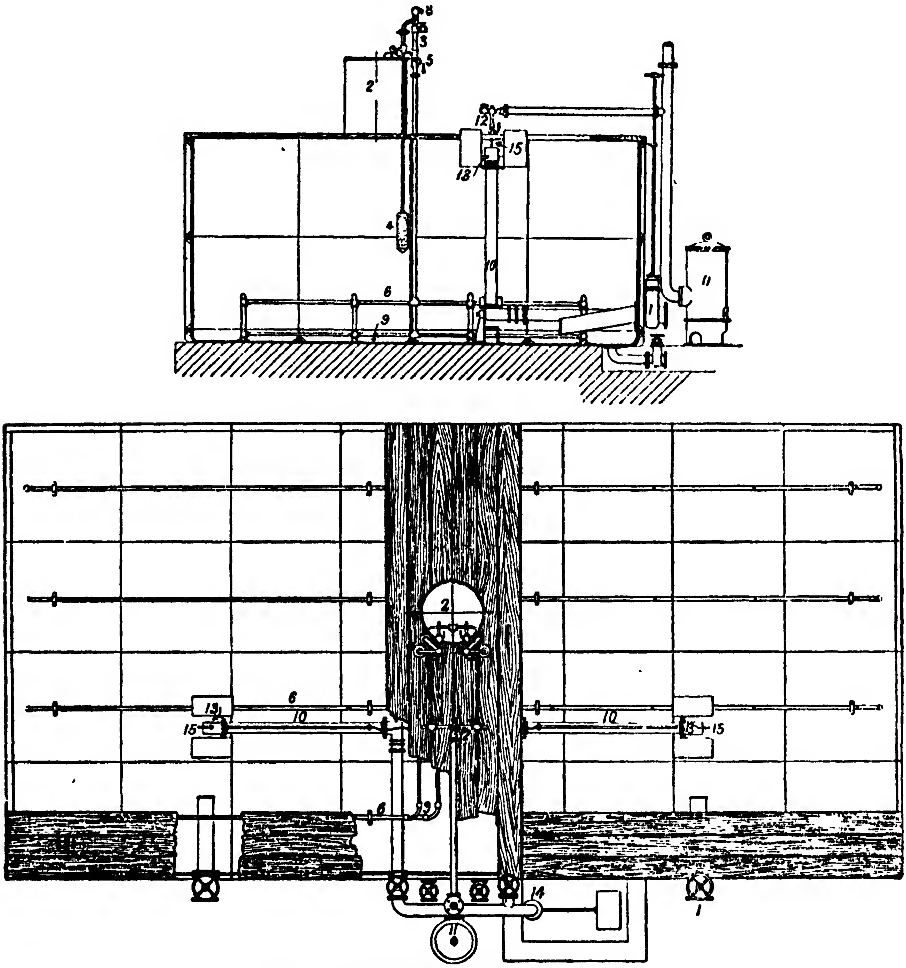


Fig. 10.—Purifier (Elevation and Plan).

way the new precipitate, which is very finely divided, combines mechanically with the coarse particles of the mud, and subsidence of the precipitate is thereby greatly accelerated.

After the blower has been in operation for about ten minutes the steam is turned off, and in about an hour the water becomes so clear that at a depth of 6 feet it will not contain on an average more than 1 grain per gallon of suspended matter. If the mud is not stirred up, as above indicated, the precipitate takes six hours or more to settle to the same extent.

Water softened at the ordinary temperature (especially if magnesium salts are present) after a period of about 24 hours (less if the temperature is higher) is liable to form a further small deposit of fine mud, consisting essentially of calcium carbonate and magnesium hydrate. This small deposit has little or no tendency to form a hard encrustation on boiler plates; but it may produce mischievous effects in feed pipes, injectors, clack boxes, &c. Archbutt and Deeley have entirely overcome this difficulty by slightly carbonating the softened water. This is effected by impregnating the softened water in its passage to the storage tank with the gases given off from a coke stove.

Fuel gas from the coke stove (11) is forced continuously by means of a small steam blower (12) into the upper end of the floating discharge pipe (10), and being caught by the descending current of water (which, in flowing down the pipe is repeatedly splashed upwards by baffles fixed at intervals along the bottom) is carried along with the water through the ball tap (14) fixed over the small supply tank, into which the softened and carbonated water falls, whilst the residual nitrogen, &c., of the fuel gas escapes into the air. A gauge mark on the side of the softening tank, about 2 feet from the bottom, indicates the level below which the water is not drawn off. Shortly before the water reaches this level the further descent of the discharge pipe is stopped by a "rest" fixed on the bottom of the tank.

Methods for the analysis of water are given in Part XI.

Purification of Refuse Water.—Of late years much attention has been given to the purification of trade effluents; but the problem is still one of considerable difficulty. In dye-houses where so many different operations are carried out, the composition of the waste water varies greatly from hour to hour. At one time it may be acid, at another alkaline. It may be heavily charged with impurities, or it may be comparatively clean water. Although often highly coloured, waste waters from dye-houses are not very obnoxious. They are generally free from any considerable quantities of materials capable of producing putrefaction. The worst waters, as a rule, come from the scouring department, and these are often treated separately for the recovery of the fatty matter. Refuse waters from dye-houses contain many substances which neutralise and precipitate one another; for example, dyestuffs, tannins, and metallic salts; soda, lime, and sulphuric acid. If sufficient space be available for a series of subsidence tanks, the effluent, after the whole of the waters have been mixed and allowed to settle, will often be found to contain but little impurity. Generally speaking, however, it will be necessary to employ some precipitating process. Lime is almost invariably used in conjunction with one or more of the following substances:—magnesium chloride, aluminium sulphate, ferrous sulphate, ferric sulphate, ferric chloride. At the large dye-works of Messrs. Spindler * near Berlin, where 10,000 cubic metres (about 2,200,000 gallons) of waste waters are treated daily, lime and magnesium chloride are used as precipitating agents. In the *Proceedings of the Institute of Civil Engineers* † (1895, p. 123), W. Naylor described a plant used by Stanning & Sons, of Leyland. The bleach and dye-liquors, along with the wash waters, are mixed with lime and alumino-ferric sulphate in a channel on their way to the precipitation tanks in which subsidence of the suspended matters takes place. The almost clear liquor is conducted away from the top of the tanks by floating arms, and the sludge is removed by a Shone ejector, into which it gravitates. A volume of 500,000 gallons is dealt with daily, this being the combined capacity of the tanks. The quantity of alumino-ferric sulphate used per day amounts to 466 lbs.

In a paper entitled "The Purification of the Waste Water from Print-

* *Journ. Soc. Dyers and Col.*, 1889, p. 154.
† *Journ. Soc. Chem. Ind.*, 1896, p. 46.

works," R. J. Flintoff * describes an arrangement for treating 20,000 gallons of waste water daily, giving 36 hours complete quiescence, or 60,000 gallons with 16 hours rest. The plant consists of three precipitating tanks, each 30 feet long, 12 feet wide, and 9 feet deep; four effluent filters, each 28 feet long, 14 feet wide, and 3 feet deep; two sludge filters, each 28 feet long, 20 feet wide, and 3 feet deep; and two sludge tanks, each 20 feet long, 8 feet wide, and 8 feet deep. The sludge filter is composed of cinders, clinkers being placed at the bottom, and the filter filled up with strata of particles of decreasing size. Cinders or gravel may also be used for the effluent filters, but Flintoff prefers ferric oxide obtained from burnt pyrites in the manufacture of sulphuric acid. The oxide of iron is covered with gravel about the size of peas, and finally a layer of sand about an inch deep is thrown over the gravel. Instead of keeping the soapy waters separate, Flintoff prefers to run all together with washing waters as well through the purification arrangement. The water is run into one of the sludge tanks where much of the insoluble matter subsides, and the fatty scum which collects is retained. The liquid from this tank, taken from a point between the scum and sediment, is directed into one of the precipitating tanks, and when full treated with a precipitant, the water being sent into the next tank. The water in the tank to be treated is thoroughly mixed by forcing air through a pipe for that purpose. A sample is withdrawn and tested. If acid, milk of lime is added until alkaline. A solution of basic ferric sulphate, containing 5 to 10 per cent. aluminium sulphate is then slowly poured in until a precipitate forms in large flakes. This is ascertained by taking samples in glass cylinders. The pumping is now stopped, and the tank allowed to remain at rest for a period of 16 to 36 hours as required. The water is treated the same way in the other tanks in turn. When the third tank is being filled the contents of No. 1 tank are run on to the effluent filter. So that, at any given time, one tank is being filled, one standing, and another discharging its contents on the filter. The sludge tanks require emptying once a fortnight, but the precipitating tanks need only to be "sludged" out once every two or three months.

The "Archbutt-Deeley" apparatus for softening water, described on p. 83, forms a plant eminently adapted for the purification of trade effluents. It is made by Mather & Platt, Limited, and many dyers, bleachers, and calico printers in Lancashire, Yorkshire, and Scotland have adopted the system. In the *Journal of the Society of Dyers and Colourists* (1895, p. 219), a description is given of this process in treating the refuse waters from the dye and bleach works of Mr. Joseph Jackson, Smedley, near Manchester. The reagents used were milk of lime and a solution of ferrous sulphate. By means of two tanks, each having a capacity of 40,000 gallons, the waste water was purified at the rate of 20,000 gallons per hour.

* *Journ. Soc. Dyers and Col.*, 1897, p. 99.

PART IV.

WASHING AND BLEACHING.

As they come into the market the textile fibres are always in a more or less impure state, and the foreign substances adhering to them have sometimes to be removed before they can be manufactured, as is the case with wool; or they may be removed from the material in the manufactured state.

The object of washing and bleaching is to remove these impurities, as well as any substances which may have been used in the process of manufacture, either for the purpose of facilitating the spinning or the weaving—*e.g.*, oil for the spinning of woollen and worsted yarns, and animal or vegetable size for strengthening the warps in weaving.

The materials employed and the processes used for the cleansing or washing and bleaching of the different textile fibres vary considerably according to the nature of the fibre, and will consequently be described separately for each.

WASHING AND BLEACHING OF COTTON.

This may either be effected before spinning, or in the yarn or in the piece; most cotton goods are bleached in the piece.

Crude cotton contains, besides hygroscopic moisture, about 5 per cent. of impurities, most of which are insoluble in water, but soluble in alkalies or acids. By boiling cotton in soda ash for seven or eight hours, and adding excess of dilute sulphuric acid to the resulting dark brown liquor, a copious, light brown, flocculent precipitate is obtained, while the liquid remains nearly colourless. This precipitate, which contains the principal impurities in the cotton, has been made the subject of a careful study by E. Schunck. When dried it forms a brown, brittle, horn-like mass, translucent at the edges, which leaves, when incinerated, 2·3 to 6·9 per cent. of a light yellow non-alkaline ash. By suitable treatment, Schunck was able to isolate from this residue the following substances:—

1. A wax-like body, which he called *cotton wax*, strongly resembling the wax obtained from the leaves of the Carnauba palm. It is lighter than, and insoluble in, water; but soluble in alcohol and ether. It has a waxy lustre, is translucent, friable, and does not soften when kneaded between the finger and thumb. Treated with boiling dilute caustic soda, it melts without dissolving, and the filtered liquid gives only a trifling precipitate with acid.

The fact that raw cotton, or materials made from it, are so difficult to wet out is probably due to the presence of a thin coating of this peculiar wax on the surface of the fibres.

2. A *fatty acid*, which melts at 55·5° C., and which appears to be either margaric or a mixture of stearic and palmitic acids.

3. Two nitrogenous, amorphous, brown *colouring matters*, one of which is easily soluble, the other sparingly soluble in alcohol. The darker shade of colour, seen in the so-called "nankin" cotton, is probably due to a great excess of these colouring matters existing in the fibre.

4. *Pectic acid*, which was obtained in the form of a light yellow amorphous substance resembling gum or gelatine. It dissolves in water to a clear and colourless solution, which reddens blue litmus. The substance is precipitated from its aqueous solution by acids and most metallic salts. Its compound with ammonia is precipitated from aqueous solution by neutral salts like sodium chloride or ammonium chloride.

5. Albuminous matter.

Of these various bodies, the pectic acid far exceeds the others in quantity; then follow the colouring matters. The three other constituents are present in extremely minute quantities only (*Schunck*).

The aqueous extract of raw cotton has been examined by Lester.* It is a brown deliquescent substance, and is present in amounts varying from 1½ to 2 per cent. of the weight of the fibre. When extracted with benzene, raw cotton yields 0·5 to 1 per cent. of a brown wax-like substance. Raw cotton also contains about 1 to 2 per cent. of ash, most of which is removed in the process of bleaching. Schindler found in raw Egyptian cotton 0·25 per cent. nitrogen, which would correspond to about 1 6 per cent. albuminoid substance.

The removal of these various impurities is effected by the process of bleaching, which was originally effected by steeping or boiling the goods in potash, and then leaving them spread out on the grass. The effect of the alkaline treatment was to remove the bulk of the impurities, the remaining colouring matter being destroyed by the joint action of light and air. Lime, soda ash, or caustic soda have now taken the place of potash in the first treatment, which is technically known as "bowking" (Germ.. *Bäuchen*), while for the destruction of the colouring matter the more convenient treatment with an artificial oxidising agent (usually bleaching powder) has superseded the exposure to light. Another operation to which cotton goods are subjected during the bleaching process is that of "souring," which consists in a treatment with cold dilute sulphuric or hydrochloric acid, and which usually follows the lime boil or the treatment with bleaching powder (chemicking). In some of the modern processes of bleaching, a treatment with cold or hot acid precedes the other operations.

It is commonly supposed that the strength of cotton goods is slightly impaired by the process of bleaching. But although this is frequently found to be the case, it has been conclusively proved, by means of quantitative measurements, that a well-conducted bleaching process actually increases the tensile strength of cotton goods.

RAW OR LOOSE COTTON.

Loose cotton intended for spinning is seldom bleached, since there is little demand for this article. The processes employed for the purpose must be such as not to impair the spinning properties of the fibre, and it is consequently essential that its natural lubricant, the cotton wax, should not be removed. Any undue matting of the fibres, especially in the alkaline treatment, should also be guarded against. The latter difficulty can be obviated by the use of apparatus like that of Obermaier, which are constructed for the dyeing of loose cotton, and which may be covered with lead inside to prevent the action of the reagents used in bleaching.

* *Journ. Soc. Chem. Ind.*, No. 6, 1902.

Sansone * recommends the following process, which, he states, gives excellent results:—

1. The cotton is first worked until thoroughly impregnated in a bath of sodium hypochlorite containing a small amount of carbonate, and standing at 2° to 4° Tw. until thoroughly impregnated, when it is allowed to steep for three to four hours, or even overnight. It is then taken out, left to drain, and washed.

2. It is then transferred to a bath containing bisulphite of soda at 2° to 3° Tw., worked for an hour, and washed.

If the cotton is not perfectly white the operations may be repeated.

According to J. Persoz † good results are obtained in bleaching loose cotton, sliver, or very fine yarns by the process of Leblois, Piceni & Co. The process consists essentially of two treatments, viz.:—(1) Extraction with very weak soda lye or even water only; (2) treatment with a solution of hypochlorite of soda. This latter is obtained by grinding bleaching powder with an equivalent quantity of caustic soda. The clear solution is used at a strength of $\frac{1}{4}$ to $\frac{1}{8}$ per cent. available chlorine.

In the bleaching of cotton (principally cotton waste) for gun cotton or for cotton wool,‡ much more drastic treatment is permissible. The material is usually first extracted with benzine or some other suitable solvent, boiled with caustic soda and resin soap, and then bleached with bleaching powder. It is subsequently soured and washed until neutral.

COTTON YARN.

When it is to be dyed subsequently in *dark colours*, cotton yarn is simply boiled in water or allowed to lie over night in soda ash for the purpose of removing the greasy impurities, which would otherwise render the even wetting out of the fibres difficult.

For the bleaching of cotton yarn a more complicated process is necessary. The principal operations are:—*Boiling* in caustic soda or soda ash; *bleaching* in chloride of lime; *souring* in hydrochloric or sulphuric acid; and, lastly, for white yarn, *washing* and *blueing*. This is, in principle, the method adopted in nearly all bleaching processes, but the details (strength of solutions, duration of treatment, &c.) not only vary in different works, but in one and the same works, according to the quality of the cotton and the yarn to be bleached. The harder the twist the more difficult is the yarn to bleach, and with hard spun Egyptian yarns it is necessary to repeat some of the operations.

The addition of a small amount of soap or Turkey-red oil to the contents of the kier has the effect of removing the waxy impurities, thus causing more rapid and thorough wetting out, and giving rise in most instances to a better bleach.

The following particulars may be taken as typical:—

1. Boil 6 to 12 hours in low-pressure kier in soda ash (4 per cent. of weight of yarn).
2. Wash in open vessels; 2 turns.
3. Chemick, 2° Tw., 6 to 8 hours in circulating cistern.
4. Wash in cistern with water; 10 minutes.
5. Sour in another cistern for 15 minutes with sulphuric acid at $\frac{1}{2}$° to 1° Tw. If iron stains are present, use hydrochloric acid of the same density instead of sulphuric acid. Run off sour.
6. Wash in cistern; 3 waters.
7. Soap, hydro-extract, and dry. With twofold yarns use blue in the soaping.

For small lots the following process gives good results:—Boil two to three hours with caustic soda of 2° Tw. and 2 per cent. soap; wash, steep for one to

* *Dyeing*, p. 45. † Jury's Report on the Paris Exhibition, 1889.
‡ See also F. B. Kilmer, *Journ. Soc Chem. Ind.*, 1904, p. 967.

two hours in chloride of lime at 1° Tw.; wash and sour in hydrochloric acid at 2° Tw.; steep one hour; wash and soap.

The boiling with soda or caustic soda is usually effected in open or low-pressure kiers, but in some works high-pressure kiers, similar in construction to those used for pieces, are preferred. On the other hand, low-pressure kiers are frequently used for pieces, especially in "market" bleaching. Fig. 11

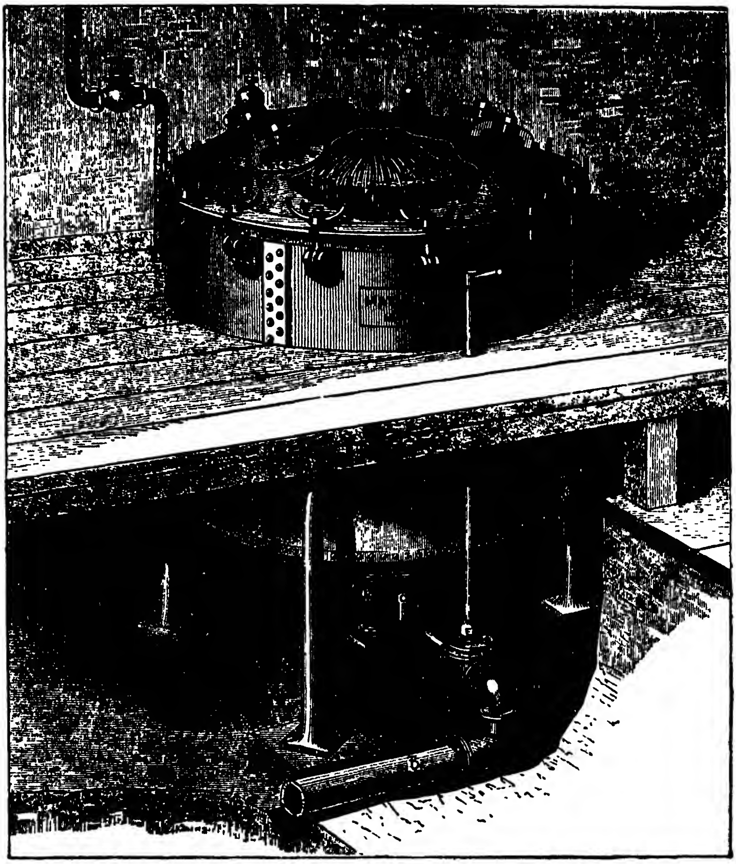


Fig. 11.—Low-pressure bleaching kier.

shows the general appearance of a low-pressure kier, part of the lid being broken away in order to show the puffer pipe in the interior. It is constructed to work at a pressure of 5 lbs. When filled with yarn, the liquor (soda ash or caustic soda) is run in from above, the lid screwed down, and steam turned on at the valve. The steam passes through the injector, B, at the bottom of the kier, drawing with it the liquor which has collected underneath the false bottom. This is thus forced up the pipe in the centre, and showered over the goods, through which it percolates and collects again under the false bottom. D is the waste pipe through which the liquor is let off by the valve, E, when the operation is finished.

The chemicking, souring, and washing off are usually done in a simple arrangement (Fig. 12), by means of which much hand labour is saved. This

consists of a stone or wooden cistern, A, provided with a false bottom, into which the yarn is laid or packed evenly, so as to insure an even circulation.

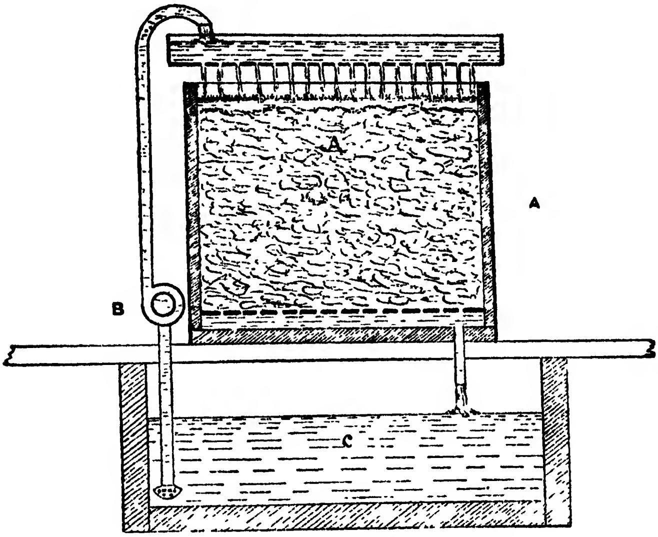


Fig. 12.—Cistern for yarn bleaching.

The liquor with which the yarn is to be treated is raised by means of a centrifugal pump from a well below the floor line in which it is stored, and caused to

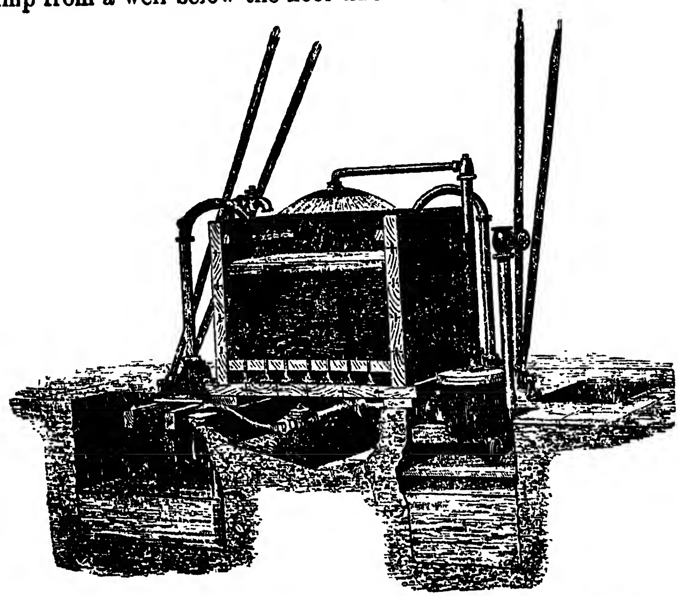


Fig. 13.—Mather & Platt's improved arrangement for yarn bleaching.

be thrown over the goods, through a perforated wooden tray. After percolating through the goods it accumulates below the false bottom, and flows back

into the well again. The strength of the liquor must, of course, be kept up by additions which are made from time to time.

The final washing of the yarn must be carefully effected in order to eliminate the last traces of acid, which, if left in, would cause tendering. There is no doubt that the alkalinity of the water used in this operation is of considerable importance, and that it brings about, in the great majority of cases, the neutralisation of the last traces of acid in the goods. With water of exceptional purity, therefore, a larger amount would be necessary than with water showing an ordinary amount of temporary hardness.

In the improved arrangement of Mather & Platt (Fig. 13), the operations of boiling with alkali, chemicking, souring, and washing are all done in one and the same apparatus without moving the material, and thus a great deal of labour is saved, the handling of the material being reduced to a minimum. The apparatus consists, as before, of a wooden cistern provided with a false bottom, into which the yarn is evenly packed. The caustic soda lye is caused to circulate through a steam injector, being drawn from below the false bottom, and sprayed over the top of the cistern through a nozzle. After having been boiled for a sufficient length of time the lye is let off, the goods are washed with water, after which there follows the treatment with bleaching-powder solution, which is drawn up from the well and showered over the goods by means of a centrifugal pump. The souring is effected in an analogous manner.

Washing and blueing are only necessary for yarn which is to remain white. The operation is usually carried out in wash stocks, as shown in Fig. 14. The

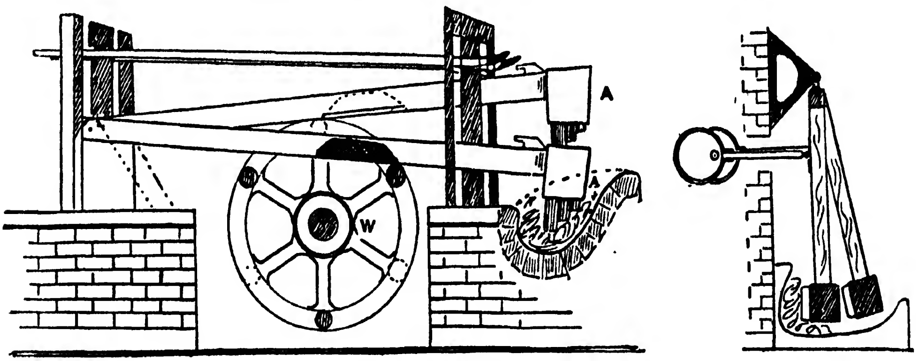


Fig. 14.—Wash stocks.

yarn is placed in a cavity, where, impregnated with soap and blue, it is subjected to the thumping action of the large wooden hammer, A, which is caused by the rise and fall of the arms carried by the slowly-revolving wheel, W. According to another method, the washing and blueing are done continuously by tying the hanks loosely together, end to end, with short pieces of string, and passing them thus in rope form several times up and down through a bowl containing the soap solution and blue, and, lastly, between two heavy wooden rollers covered with cotton rope, the upper one of which lies with its axis in a slot, so as to press with its own weight only on the yarn, rising and falling as each hank passes through.

After washing and blueing, the goods are hydro-extracted and dried.

BLEACHING IN THE COP.

Cotton yarn is bleached to some extent in the cop, as it comes from the spinning frames, in order to avoid the time and labour required for reeling it into hanks. The bleaching may be conducted in the same way as for hanks, but with this difference, that in the boiling process the cops are packed in coarse linen bags. The operations may also be conducted in apparatus like those in use for dyeing by the packing system (*q.v.*). If the apparatus is constructed of iron, it should be lead-lined, and pipes, pumps, &c., should be made of hard lead or gunmetal.

According to A. Schott,* it is advantageous to treat the cops after boiling in the kier with sulphurous acid, in order to remove the impurities which are soluble in the lye, but which would be precipitated by dilution. The goods are then chemicked.

COTTON PIECE GOODS.

The bleaching of cotton in the piece by far exceeds in importance that of bleaching in the yarn. Before the introduction of chlorine as a bleaching agent, the operations of bleaching were simple but tedious; and consisted in boiling the goods in potash, steeping in buttermilk, and exposing them to the sun and air in fields. The introduction of sulphuric acid in place of buttermilk was regarded as a great improvement, reducing the time required from six to three months. Chlorine, which was discovered by Scheele in 1774, was first suggested as a bleaching agent by Berthollet in 1785, and was used shortly afterwards on a practical scale by James Watt. The introduction in 1799 of bleaching powder by Charles Tennant greatly facilitated the use of chlorine as a bleaching agent. In the year 1835 the following process was (according to Ed. Schwartz) in common use:—Steep for twelve hours in cold water; wash in stocks; boil in lime; rinse, and boil twice in caustic soda for ten to twelve hours (using up to 2 lbs. caustic soda to 100 lbs. goods); spread on grass for six to eight days, or chemick and sour; boil twice with caustic soda as above, bleaching again after each operation, and ultimately rinse first with hot and then with cold water. The repeated boiling with caustic soda was necessary, because the goods were not soured after the lime boil, and the lime soaps consequently remained on the fibre. In spite of the numerous treatments, the results were uncertain, and frequently faulty. By the introduction, at a later date, of soda in place of caustic soda, these insoluble lime soaps were acted upon, yielding soluble soda soaps, and leaving calcium carbonate on the fibre. Souring after the lime boil was also resorted to, in order to decompose the lime soaps, and these altered conditions severally served to render the process certain and effective. These improvements were introduced about the year 1837, and between this date and 1840 a further improvement—viz., boiling under pressure—took place. With slight modifications, this process is still largely employed.

The Old Madder Bleach†—The following is a general outline of the process, as used for goods which are subsequently to be printed:—

* German Patent No. 88,945.

† The term "madder bleach" dates from the time when madder was largely used in the dyed style in printing. In principle this consisted in first printing on the pattern with thickened mordants of red liquor and iron, or mixtures of these two, and, after ageing and fixing, dyeing the whole piece in madder. In this manner reds, pinks, violets, chocolates, &c., were obtained of great fastness and beauty. The great difficulty, however, was to obtain a clear white ground, for, although the goods may have been perfectly white to begin with, the madder stained the unmordanted parts, and much difficulty was afterwards experienced in clearing them. By the use of resin soap, this difficulty was got over, and this particular treatment distinguishes the madder bleach from other bleaching processes.

1st	Operation,	Singeing.
2nd	„	Grey washing.
3rd	„	Boiling with lime under pressure.
4th	„	Treatment with weak acid.
5th	„	Boiling with resin soap under pressure.
6th	„	Boiling with soda ash under pressure.
7th	„	Treatment with chloride of lime.
8th	„	Treatment with weak acid.
9th	„	Final washing and drying.

From this it will be seen at a glance that the bleaching of cotton pieces is a more complicated process than the bleaching of yarn. This arises from the fact that in cotton yarn we have simply the natural impurities of the cotton fibre to deal with, no additions being made during spinning. In cotton pieces, however, we have, in addition to these, the accidental impurities, such as grease from the machinery, finger marks, but principally the constituents of the size almost invariably employed for strengthening the warp before weaving. The size used for this purpose may contain a large variety of substances, such as farina (starch), soap, tallow, paraffin wax, &c. Small quantities of lime soaps, compounds of copper, iron, and earthy matters may also be present in the material. Some of these impurities are removed by water alone, others by alkalies and soap, and the rest, with the exception of the natural colouring matter of the cotton, by acids. The removal of the natural yellow colouring matter of the cotton, or the bleaching proper, is usually effected by means of chloride of lime. Mineral oil stains and paraffin wax (unless accompanied by a certain proportion of natural fat or oil) are, however, not removed by any of these treatments, and are frequently the cause of great trouble to the bleacher, dyer, and finisher. For their removal in the process of bleaching, Ed. Schweizer* recommends boiling the goods with soap and aniline oil, using the latter in the proportion of 12 to 15 litres for every 200 pieces, or the goods may be boiled for half an hour with 100 grms. aniline oil per litre of oleïn soap. In place of aniline oil, phenol can be used in the proportion of 5 kilos. phenol per 2,000 kilos. of pieces.

Marking and Stitching.—When brought to the works, the goods are deposited in the grey-room, where they undergo the preliminary operation of marking with tar or some other indelible coloured substance for the purpose of recognising the various lots afterwards and of tracing faults. They are then stitched together, end to end, by means of special sewing machines (chain-stitch), and pass from the grey-room through guides or "pot-eyes" into the bleaching croft in continuous rope form, which shape they retain throughout the bleaching operations.

Singeing.—This operation is generally employed for those cotton goods which are afterwards to be printed; but it is also used extensively for other goods, such as unions, linings, corduroys, &c. The object of singeing is to remove, as far as possible, all the loose hairs from the surface of the cloth, and thus give it a clean face.

Singeing is effected in three ways, viz.:—

1. Plate-singeing.
2. Singeing with revolving rollers.
3. Gas-singeing.

* *Journ. Soc. Dyers and Col.*, 1896, p. 209.

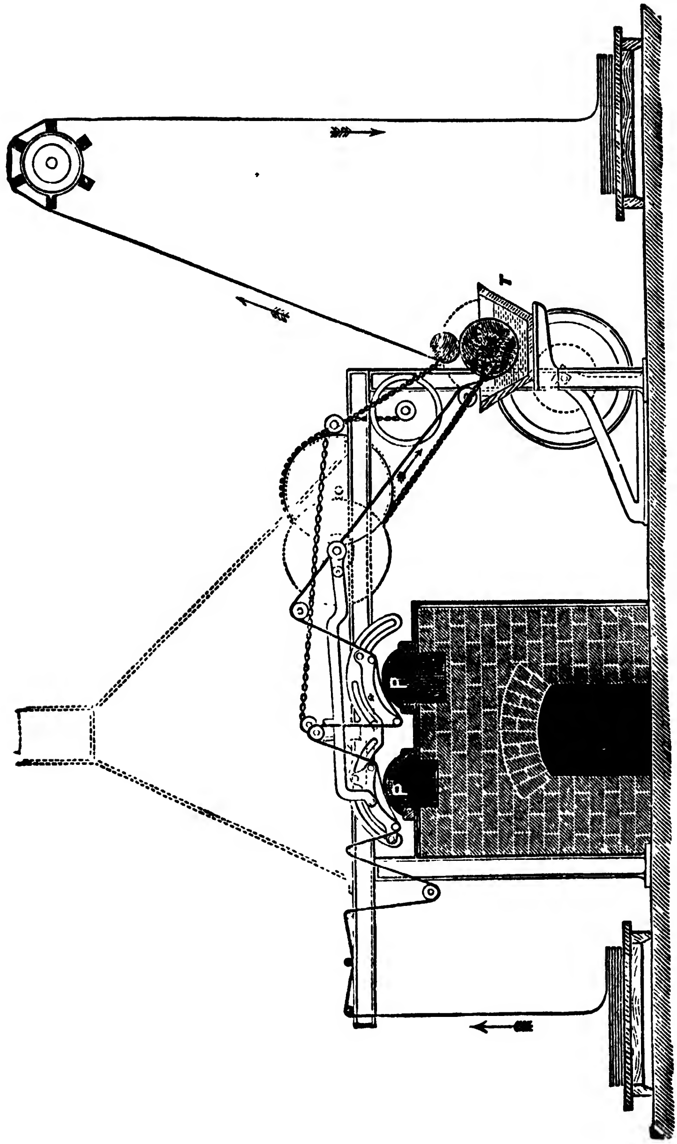


Fig. 15.—Plate-singeing stove.

In plate-singeing the pieces previously stitched together, end to end, in the grey-room are drawn at a rapid rate over two arched copper plates, P, P, which are kept at a red heat by direct fire, and thence through a water trough, T, to extinguish sparks.

An improvement on the old-fashioned plate-singeing arrangement is the patent traversing movement of Messrs. Mather & Platt, which is shown in Fig. 15, and on an enlarged scale in Fig. 16. In the older arrangements the pieces are depressed against the plates by causing them to pass underneath a bar or rail between the two plates. A serious drawback to this system is the fact that the cloth touches in its passage only one part of the plate, which is thereby rapidly cooled. To keep up the heat at this place of contact a large amount of fuel is wasted, and the portion of the plate not touched becomes unnecessarily hot, its life being thus considerably shortened. In the traversing arrangement, the rails which depress the cloth on to the plates are continually moving to and fro and this enables the whole surface of the plate to be utilised. The working of the system will be sufficiently clear from the figure.

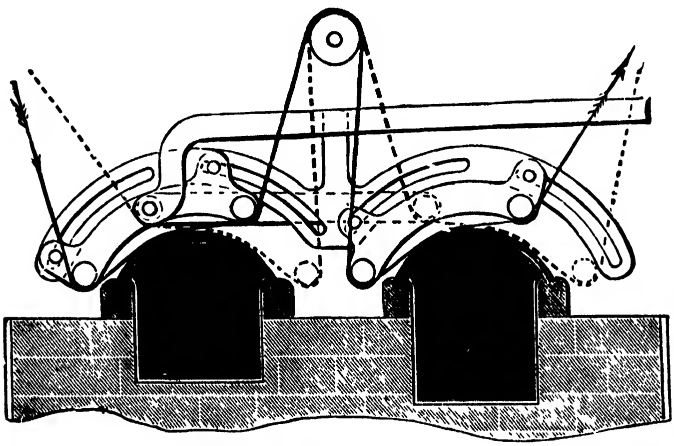


Fig. 16.—Traversing movement.

The rate at which the pieces pass over the plates is regulated by admitting more or less steam to the donkey-engine driving the rollers. Union goods are usually beamed off the singe-plates. A hood, indicated in the figure by dotted lines, serves to carry away the burnt products.

In the roller singeing machine, the plates are substituted by a hollow cast-iron cylinder, R (Fig. 17), which is flanged at each end and rests with its flanges on toothed rollers, A, A, which are caused to revolve slowly by the worms, W, W. The cylinder is thus caused to revolve slowly in a direction opposite to that followed by the pieces. The whole flame of the furnace passes through the roller into the flue on the other side, heating it to a uniform red heat. By such an arrangement the pieces come into contact with a continuously renewed surface of the roller and the singeing is more regular. Besides this, the pieces can be singed twice on the same side in one operation. The course of the pieces is shown in the figure by arrows.

Singeing by means of gas is more convenient, but more expensive, than either of the foregoing methods, and is necessary for figured goods, corduroys, &c., on account of the unevenness of the surface. Formerly the flame was drawn right through the material, and this method, though having been

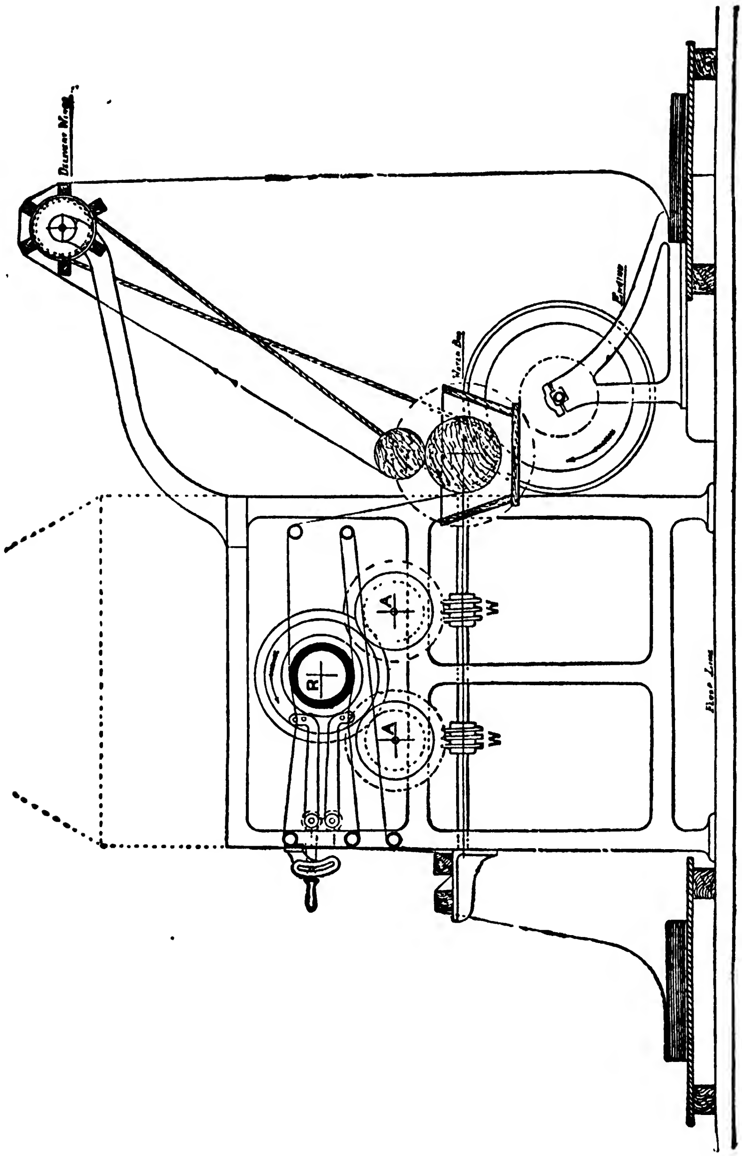


Fig. 17.—Patent singeing machine with hollow revolving roller. Scale $\frac{1}{12}$ natural size.

abandoned, since it was found to impoverish the fabrics, has recently been re-introduced (see below). In the present system of gas-singeing, the pieces are passed over rollers of small diameter while being exposed to the action of a Bunsen gas flame, thus causing the "nap" to stand out as much as possible.

Figs. 18 and 19 show two different arrangements for singeing by gas. In the first, the pieces, after having passed over the rails, R, pass under the nap roller, N, directly underneath which there is a row of Bunsen burners. Thence they pass under the second nap roller, N^1, to another row of Bunsen burners, which are so placed as to singe those parts left in between the burners of the first row.

In the second arrangement a similar principle is adopted, but the material is brought twice into contact with the same flame. The burnt products are drawn off by the hood, H, which runs across the whole breadth of the machine.

The gas, previously mixed with the necessary quantity of air for its combustion, is supplied to the burners under pressure from a Root's blower. By this method a higher temperature is produced than with the ordinary Bunsen flame, and a considerable saving in gas is said to be thus effected.

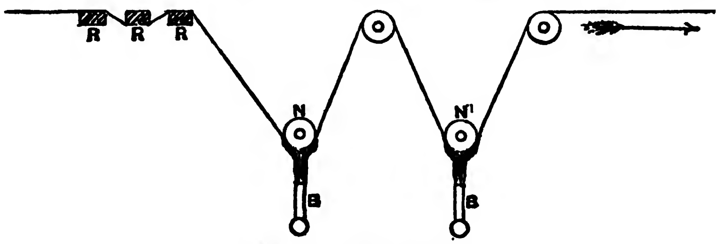


Fig. 18.—Gas-singeing.

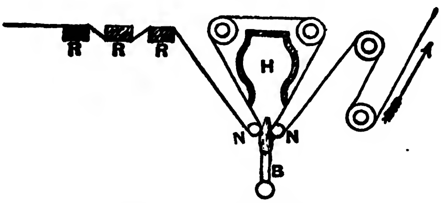


Fig. 19.—Gas-singeing.

Fig. 20 shows the construction of a double gas-singeing machine, invented by F. Binder, and made in this country by Messrs. Mather & Platt. To the right, Fig. 21, is shown an enlargement of the burner and exhausting chamber. In this the old principle of drawing the flame through the cloth has been re-introduced, but it is claimed for it that the drawback of impoverishing the cloth is done away with whilst the nap is thoroughly removed from the surface, and at the same time great economy in gas is effected.

The cloth in being singed passes across a slot, S, in the underside of an exhausting chamber connected with a fan, F, and the flame from a burner, B, below is gently drawn through the cloth by a current of air. To prevent over-heating of the exhausting chamber, the latter is surrounded by a water-jacket through which a current of cold water flows. In the machine shown in the figure, both sides of the cloth are singed in one operation.

Cotton, mercerised cotton, worsted, and spun silk *yarns* are frequently singed or "gassed" for the purpose of producing a clean yarn—*i.e.*, a yarn free from loose fibre on the surface—by passing them at a rapid rate through gas flames. The singeing of worsted yarns is known as "genapping."

Grey Washing.—This operation is sometimes omitted, not being absolutely necessary. It consists in passing the goods coming from the singe house through water in an ordinary washing machine and then allowing them to

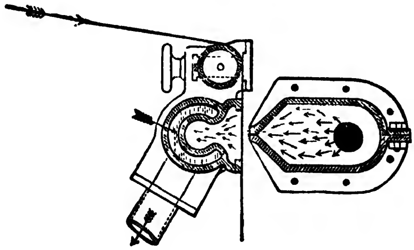


Fig. 21.

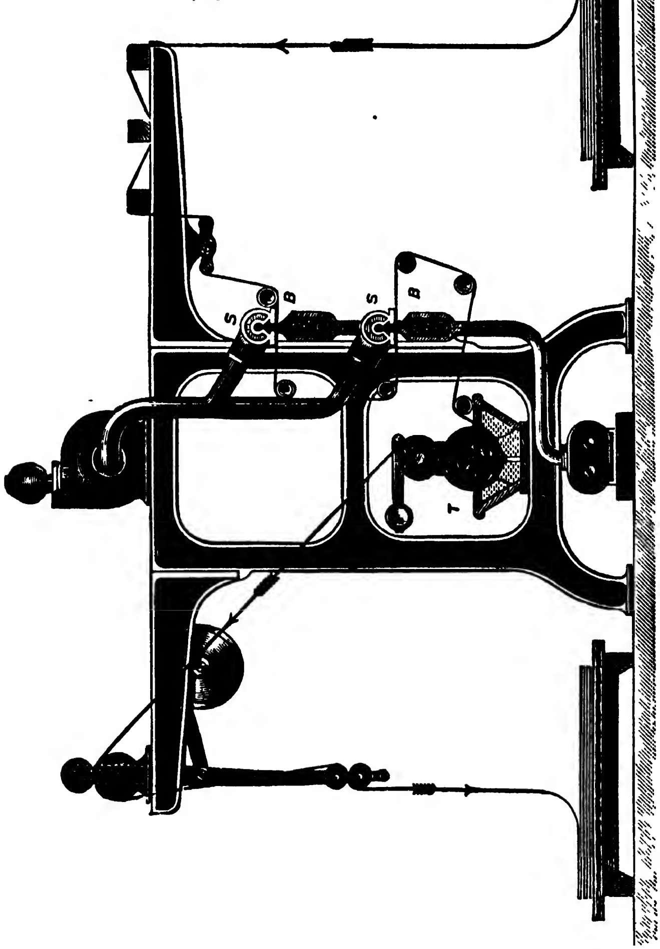


Fig. 20.—Double gas-singeing machine.

lie in a heap over-night. The result is that some of the matters soluble in water are removed; the material becomes thoroughly wetted, and much of the starchy matter becomes soluble in consequence of a fermentation which

sets in and which frequently manifests itself through a considerable rise in temperature in the goods.

Lime-boil.—In this operation the goods are subjected in kiers (large cylindrical vessels of wrought iron) to the action of lime-water, generally at a high temperature and under pressure. In all the various systems of kiers, the lime-water is caused to circulate continuously through the goods during the operation, and this is effected in various ways.

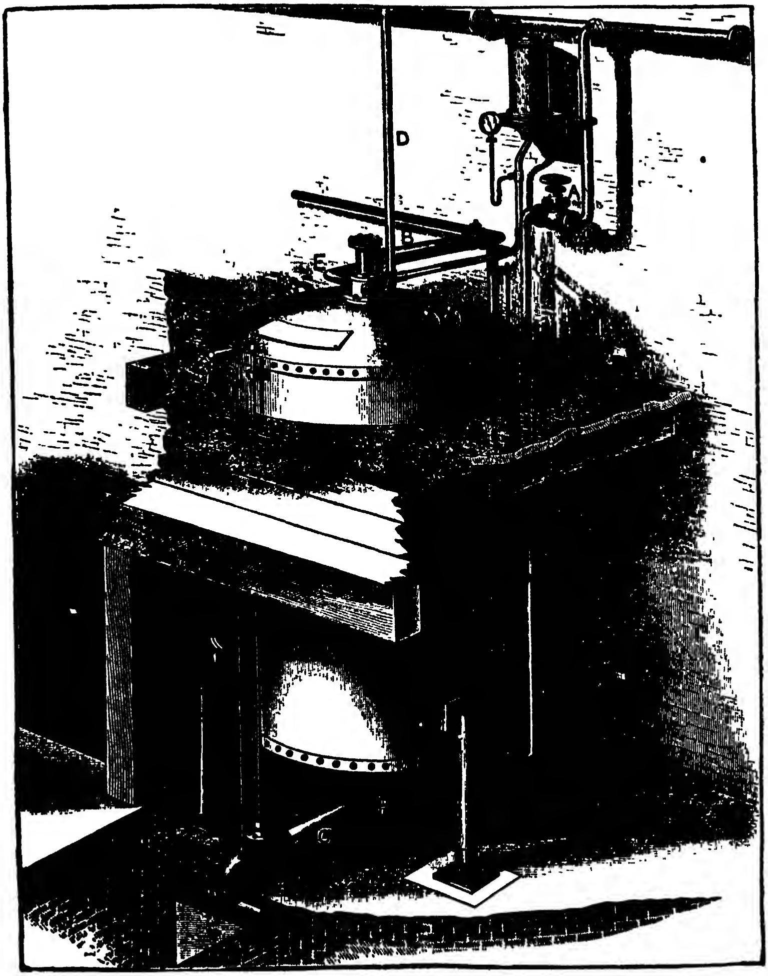


Fig. 22.—Injector-kier (Mather & Platt).

The kier in most common use among bleachers is the injector-kier (see Figs. 22 and 23); so-called because the circulation of the liquid is effected by means of a steam injector. The steam, which is turned on at the valve, A (Fig. 22), passes down to the bottom of the kier and through the injector, J, drawing the liquid through the pipe, P, from beneath the false bottom, and forcing it up to the top through the upright pipe, which conveys it through the nozzle, N, back into the kier again. Water is supplied through the

pipe, E (Fig. 23), liquor from the pipe, D, while C is the waste-pipe, which can be opened or closed from the working floor by the handle, V.

Kiers are usually constructed for quantities of cloth varying from 600 to 3,500 lbs., the diameter ranging from 1·3 to 2·1 metres, and the height from 1·8 to 3 metres. In some cases they are made larger.

In working, the calico to be bleached is first passed through milk of lime, which is made of such a strength that the material takes up about 4 per cent. of its weight of lime (CaO). The milk of lime should be passed through

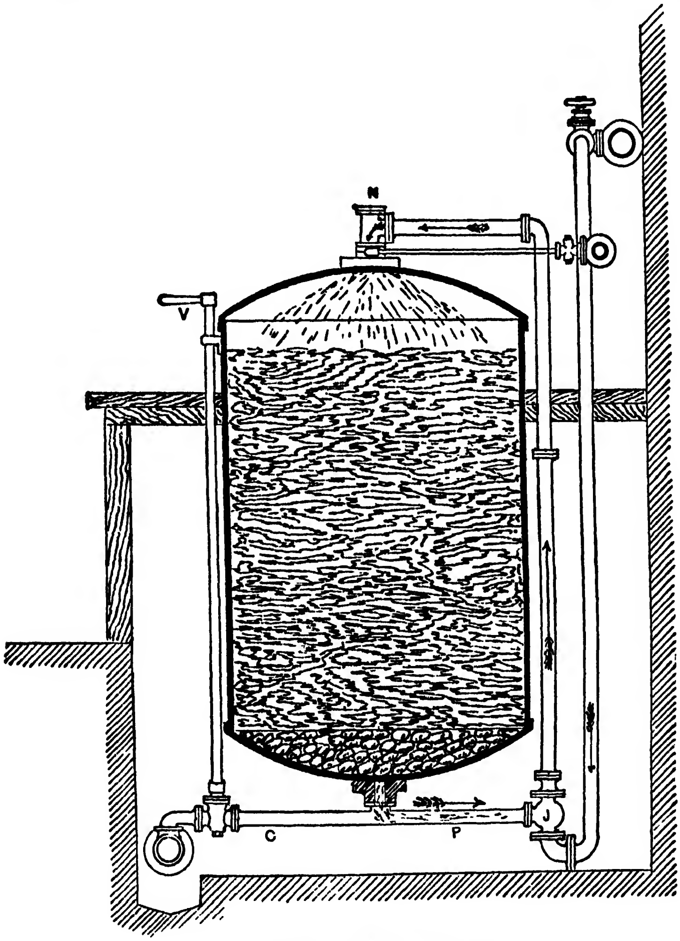


Fig. 23.—Section of injector-kier.

a sieve before use, in order to remove small stones, &c. The cloth is then packed evenly into the kier by boys, who fold it with short sticks, and then press it down by treading on it. The necessary amount of water is then run in; and, after the air has been got rid of by blowing in steam for a short time, the kier is closed, and the boiling is conducted under pressure.

The lime kiers are whitewashed from time to time on the inside in order to prevent the material getting rust stains by coming into direct contact with the iron.

After the lime-boil the liquor is allowed to blow off, so that it is necessary to fill the kier as rapidly as possible with cold water before taking the pieces out. If this is omitted, the lime-water dries on the fabric where the latter touches the hot walls of the kier, and becomes so concentrated in those places that it is but incompletely removed in the subsequent souring.

The impregnating of the pieces with milk of lime previous to their entering the kiers is effected in a machine similar to a washing machine (Fig. 24). The same or a similar machine serves for chemicking and souring.

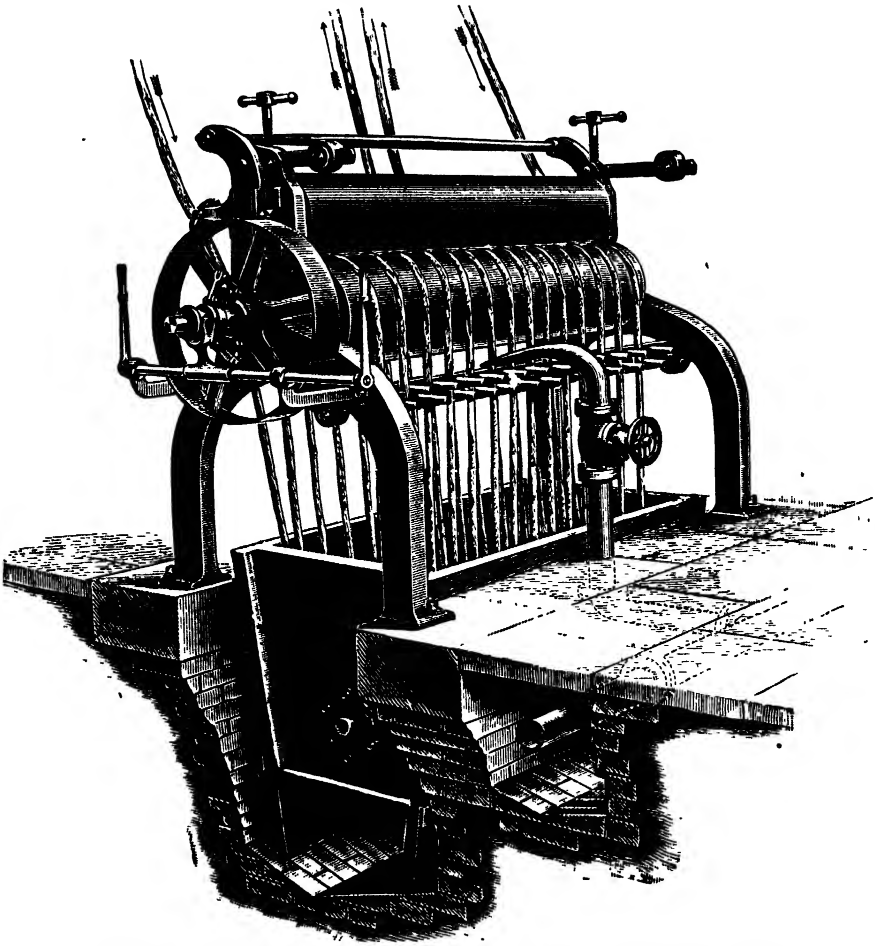


Fig. 24.—Washing machine for pieces in rope form (Mather & Platt).

The chief effect of the lime-boil is to decompose the fatty and oily matters contained in the pieces. The fatty lime soaps which are thus formed adhere to the fibre, but are completely removed in the subsequent processes. In addition to this, starchy and other soluble matters are removed, and the natural impurities are so chemically changed as to be more easily eliminated in the subsequent processes. The colour of the material is actually darker after the lime-boil than in the grey. This is especially noticeable in goods made from Egyptian cotton.

On coming from the kier the goods are washed in washing machines for the purpose of removing the soluble impurities and as much of the lime as possible before passing on to the next operation.

The washing is effected in a machine like that shown in Fig. 24, which is constructed to take two strands at once. The pieces pass in at each side through the pot-eyes, between the wooden bowls, round the roller at the bottom of the trough and up again through the bowls, and so on, being guided in their course through the machine by the wooden pegs shown in the figure. Both strands leave the machine at the centre on the side opposite to that on which they enter.

The following treatment with weak acid is known as the *grey sour* or *first sour*, and consists in running the goods through sulphuric or hydrochloric acid at 1° to 2° Tw. in a machine similar in construction to a washing machine. The souring is done cold.

The effect of the grey sour is to decompose the lime and other insoluble soaps on the fibre, and to remove metallic oxides (iron stains, &c.). The free fatty acids which result from the decomposition of the insoluble soaps remain on the fibre, but are readily removed in the next operation.

The First and Second Lye-boils.—The goods are now boiled twice with soda, generally in high-pressure kiers of the injector type (see above).

In the first lye-boil they are treated with 5 to 6 per cent. of their weight of soda ash, and 1½ to 2 per cent. of resin previously dissolved by prolonged boiling in the necessary amount of caustic soda or soda ash. Working under a pressure of 3 to 3½ atmospheres, the operation lasts from three to four hours, while with low-pressure kiers as much as twelve hours are requisite.

The second lye-boil is carried out like the first, but soda ash alone is used (1 to 2 per cent. of the weight of the material).

The effect of the lye-boils is to dissolve the free fatty acids left on the fibre after the grey sour. The effect of resin soap, which is only used for goods which have subsequently to be printed, is to remove certain constituents of the fibre which evince a slight affinity for colouring matters, and which, if left in the fibre, would leave the whites dull in printed goods.

In some works the goods are boiled with soda alone previous to the treatment with resin soap. Although not indispensable, Hummel considers this operation advantageous, since the last traces of acid left in after the washing following the grey sour are entirely neutralised, and the danger of tendering in the subsequent lye-boil with resin soap is thus averted. The addition of a very small quantity of heavy mineral oil in the lye-boil * is said to economise bleaching powder in the subsequent operation of chemicking.

After the lye-boils the goods are again washed in the washing machine. At this stage the cotton has been freed from all the impurities soluble in water, acids, alkalies, and soap-emulsion.

Bleaching.—This process, also known as *chemicking*, has for its object the destruction of what remains of the natural colouring matters in the fibre. It is effected by passing the goods through a clear solution of chloride of lime or bleaching powder, standing at ½° to 2° Tw. in a machine similar in construction to a washing machine.

After leaving the machine the goods are piled in a heap, and are preferably left exposed to the air for 12 to 18 hours before undergoing the next operation. This gives the chloride of lime time to act on the colouring matter, and it is assisted to a considerable extent during the exposure of the goods by the carbonic acid of the air, which liberates from it free hypochlorous acid:—

$$2CaOCl_2 + H_2O + CO_2 = CaCl_2 + CaCO_3 + 2HOCl.$$

* Mahien has also patented (German Patent No. 61,668) the use of coal-tar benzene for this purpose.

The *white sour*, which now follows, effects the removal of the lime from the fibre. For the white sour, either hydrochloric or sulphuric acid, at 1° to 2° Tw., is used, and the operation is carried out in the same machine as

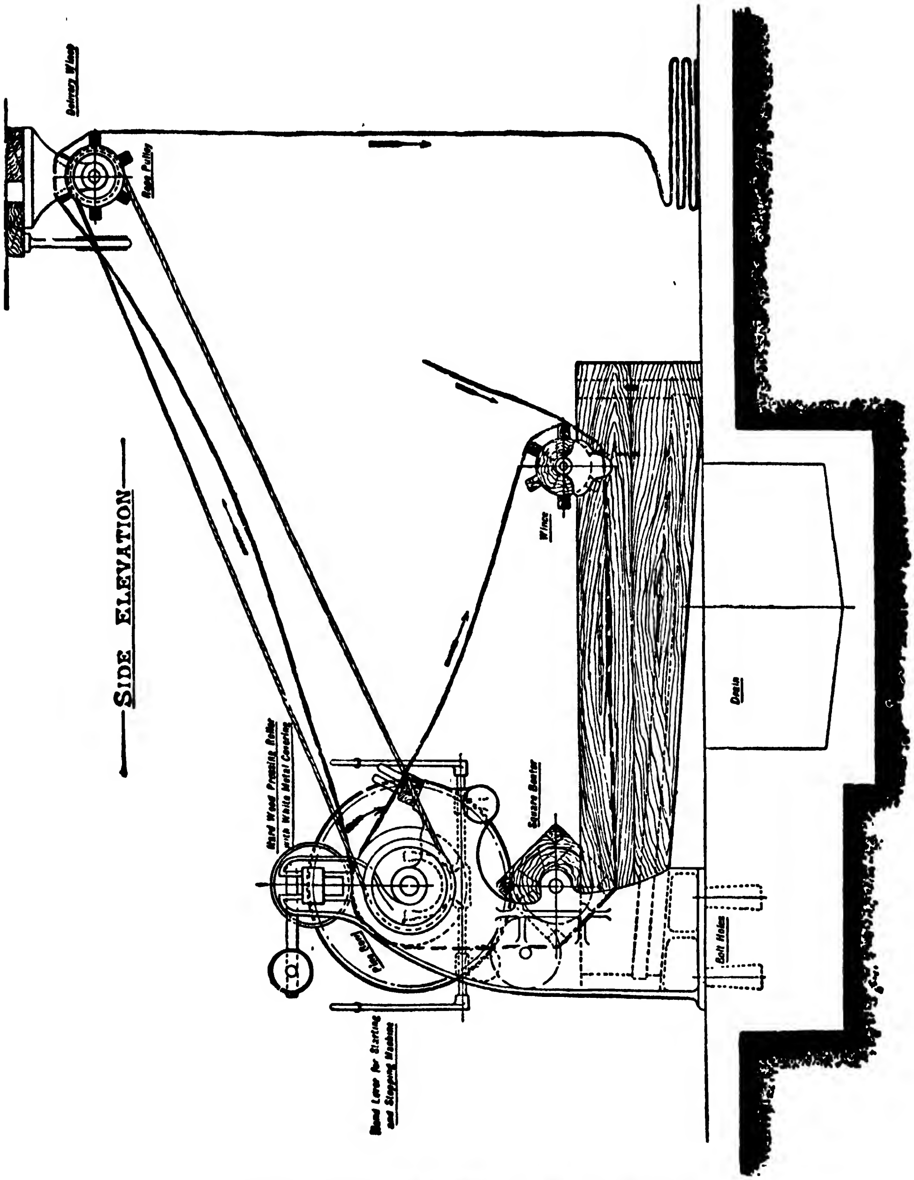


Fig. 25.—Square beater washing machine (section).

the grey sour. Some bleachers do not wash between the chemick and white sour, so that when the goods come into contact with the acid there is considerable evolution of chlorine, which acts energetically on any remaining

colouring matter. A slight economy in bleaching powder is thus effected, but it should be borne in mind that the treatment tends to produce oxy-cellulose.

The bleaching proper is now finished, and the only operations which follow are the *final washing* in washing machines, the opening out and drying over copper cylinders. It is necessary that the final washing should be carefully carried out, in order to remove the last traces of acid, which, if left in, would

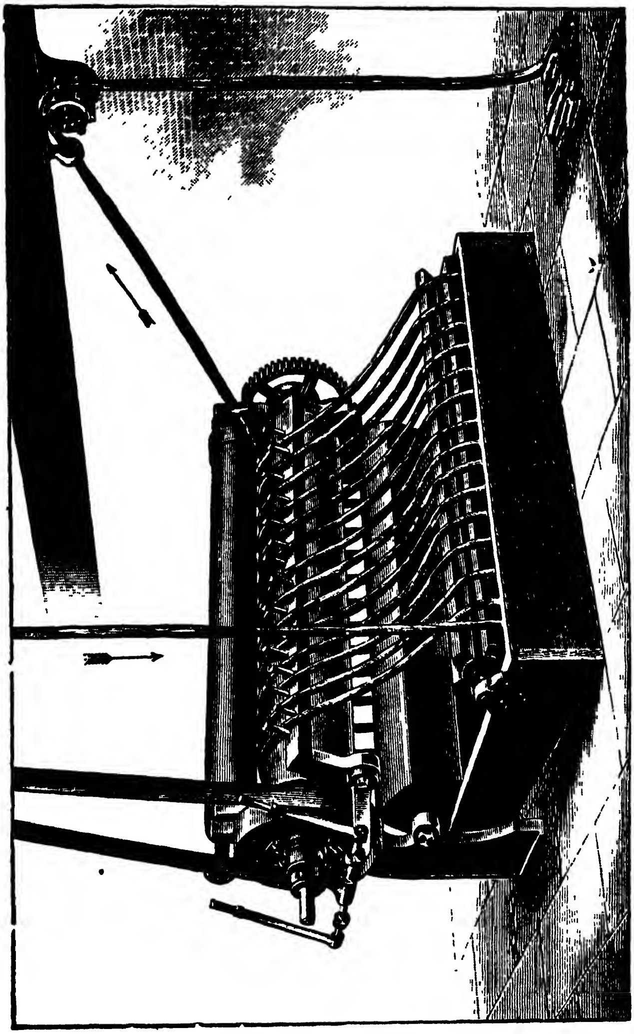


Fig. 26. Square beater washing machine.

render the fabrics liable to become tendered in the drying (see also p. 30). For the final washing, the square beater washing machine, which is shown in section and in perspective in Figs. 25 and 26, renders good service.

The final washing and squeezing may also be effected in a machine like that shown in Fig. 27, in which the goods entering the machine through a pot-eye pass between the elm bowls, B and B′, of which B is driven by pulley, D,

thence over the pine rollers, P, between the bowls again, and so on in a spiral direction until they leave the machine at the other end, as indicated by the arrows.

The following two bleaching processes are cited by Lauber (*Handb. d. Zeugdrucks*) from practice. The first is that of John Barlow, which was in use in 1872-73:—

1. Wet out in grey washing machine; allow to lie for 24 hours and wash.

2. Pass through milk of lime (400 grms. CaO for every 100 metres of calico), with little pressure on the squeezers, so that the pieces can take up as much lime as possible. It is preferable to take too much than too little

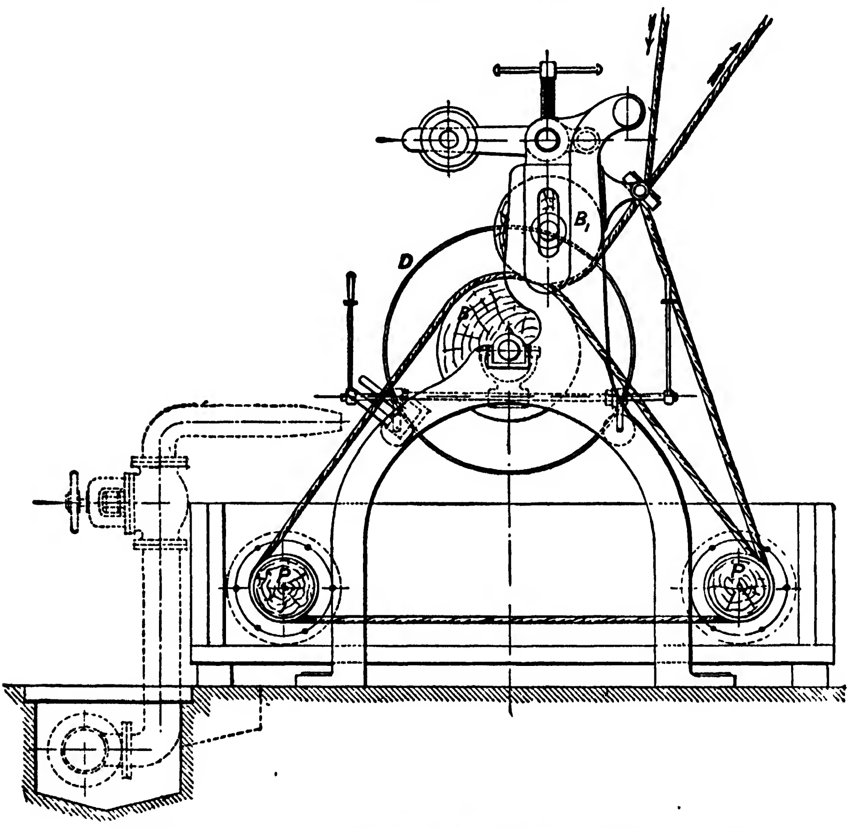


Fig. 27.—Improved bleach-house washing machine (Mather & Platt).

lime, for a properly carried-out lime-boil is the foundation of a good bleach; if it fails, the fault cannot be made good, even by using twice the usual quantity of soda and resin in the subsequent lye-boil.

3. Boil for six hours.

4. Wash twice. After the second washing squeeze well, in order to prevent the dilution of the subsequent bath.

5. Sour in sulphuric acid at 3° to 4½° Tw. Allow to lie three to four hours.

6. Wash twice. From the second washing machine the pieces are led straight into the kier.

7. Boil six hours in resin soap.
8. Wash twice. Squeeze well after the second washing.
9. Pass through chloride of lime at $\frac{1}{3}$° to $\frac{1}{2}$° Tw. Allow to lie in heaps of 20 pieces each until a good white has developed.
10. Wash.
11. Pass through sulphuric acid at 3° Tw. Allow to lie for one hour.
12. Wash twice and dry.

The following is another but a more recent process :—

1. Boil with lime for eight hours in high-pressure kiers at 2 atmospheres pressure.
2. Wash twice.
3. Sour with sulphuric acid at $4\frac{1}{2}$° Tw.
4. Wash.
5. Boil for 10 hours with soda (110 kilos. for 3,000 metres calico) at 2 atmospheres pressure.
6. Wash.
7. Chemick with chloride of lime at $\frac{1}{3}$° to $\frac{2}{3}$° Tw.
8. Wash.
9. Sour with sulphuric acid at 3° Tw.
10. Wash three times and dry.

Another process, in use in the works of Messrs. Koechlin, Baumgartner & Co., of Loerrach, with Barlow's high-pressure kiers, before the introduction of the Mather kier, is as follows :—

1. *Lime Boil.*—Pass through milk of lime (250 grms. lime for each piece) and boil under high pressure for 12 to 24 hours, according to the size of kier employed. For one holding 500 pieces, 24 hours are required, but a better result is obtained in 12 hours in a kier holding 250 pieces. Wash.

2. *Sour.*—Hydrochloric acid at 3° Tw. Allow to lie in acid for from six to eight hours. Wash twice in washing machine.

3. *First Lye-boil.*—Boil together for 10 hours 80 kilos. soda ash and 30 kilos. resin. The pieces are boiled six hours under 60 lbs. pressure with this lye, and washed.

4. *Second Lye-boil.*—Boil together for 10 hours 160 kilos. soda ash and 60 kilos. resin. Boil the pieces in the kier with this lye 12 to 14 hours under 60 lbs. pressure.

Wash well in kier, then in washing machine.

5. *Chemick.*—Chloride of lime at $\frac{1}{3}$° Tw. Allow to lie six to eight hours. Wash.

6. *Sour.*—Pass through sulphuric acid at $1\frac{1}{2}$° Tw. Wash twice in washing machine and dry.

The mean duration of the bleaching process for goods to be printed (madder bleach) is about five days.

Market Bleaching.—For goods which come into the market in the white state, the bleaching process differs slightly from that described for printed goods. The singeing is generally omitted, the lime-boil is frequently done in low-pressure kiers, and soda ash is substituted for the resin soap in the first lye-boil. In some cases, the goods are chemicked after the first lye-boil and again after the second. After bleaching, the goods are blued, either before or in the finishing. In market bleaching, the chemicking and souring are sometimes done in cisterns, as in yarn bleaching. The liquors are used over again, and a saving in material, amounting from 20 to 30 per cent., is thus said to be effected. The finishing operations are of great importance in market bleaching, and include starching, filling, damping, beetling, calendering, chasing, &c., by which both the appearance and the feel of the material may be considerably altered.

Bleaching for Turkey Red.—For goods which are subsequently to be dyed Turkey red, a full bleach is not necessary; in fact it is actually injurious, the treatment with chloride of lime preventing the production of a full bright red. This is due, according to Lukjanoff,* to the presence of oxycellulose in the bleached cotton, which prevents, to a certain extent, the proper fixation of the mordants. The process generally adopted consists in giving the goods, after boiling with water alone, either one or two lye-boils with soda or caustic soda, after which they are soured with sulphuric acid, well washed, and dried.

Better results are said to be obtained by simply boiling once under pressure with caustic soda and Turkey-red oil.

THEORY OF THE ORDINARY BLEACHING PROCESS.

An exhaustive treatise on this subject was published by M. Albert Scheurer in the *Bulletin de la Société industrielle de Mulhouse* in 1888.† According to this authority, the bleaching process takes place in two stages, viz.:—

1. The removal by saponification of the fatty matter, natural and acquired, from the material.
2. The destruction of the colouring matter.

In consequence of the protective influence which the fatty matter exerts on the natural colouring matters, it is of the first importance that saponification should take place as rapidly as possible.

The fatty bodies adhering to cotton fabrics include, besides those natural to the fibre, those acquired during the process of manufacture, such as olive, cotton-seed, palm, rape-seed, and other vegetable oils, which are more difficult to saponify, though not so difficult as tallow. The author conducted elaborate experiments, with the object of determining the conditions in boiling, favourable to the prompt and complete saponification of the various fatty bodies. These included trials with samples of unbleached, but wetted-out cloth, stained with cotton-seed oil, and with tallow, by treating them with various reagents at the boil and at 120° C. respectively. The experiments carried out at 100° with the caustic soda lye-boil, the soda, the resin soap, and alkaline-earth lye-boils, led to the conclusion that caustic soda saponifies the fats in half the time that soda does, and that there is little difference between the time taken by caustic soda of a strength of 5 grms. and 10 grms. per litre to accomplish saponification. On the contrary, there is a great difference in the case of soda, and also in the case of a mixture of caustic soda and resin. Caustic soda at 5 grms. per litre and 2½ grms. resin saponified the oil and the tallow in eighteen hours. At 10 grms. per litre, and with the same amount of resin, only one-third of the time was required. Soda ash, 10 grms. per litre, and resin, 2½ grms. per litre, did not saponify the fats any quicker than without the addition of resin. In the lime-boil, using 10 grms. lime per litre, the natural fats were saponified in six hours, and the tallow in twelve hours. With barium hydrate at 60 grms. per litre saponification is attained in three and a-half hours, but is not complete.

The experiments carried out at 120° C. showed that, in order to obtain rapid and complete saponification, it is necessary to use either the lime-boil or the caustic soda and resin boil. Although saponification was again incomplete with baryta,‡ cloth boiled with it was much clearer than when boiled with

* *Journ. Soc. Dyers and Col.*, 1886, p. 29.

† See also *Journ. Soc. Dyers and Col.*, 1889.

‡ The use of strontium hydrate for boiling, in place of lime, has recently been patented in Germany.

lime, owing to the solvent action of the former on the colouring matter of the cotton.

With regard to mixtures of fatty bodies and oils, vegetable and mineral, it was found that, when using soda or caustic soda lye-boils without resin, the time required for saponification is lengthened, since there is then only slight emulsive action, the soap needful to exercise this action being formed in very small amount, and as quickly as it is formed becoming dispersed in the lye, and thus rendered too dilute to act. But by the addition of resin amounting to 2½ grms. per litre a sufficient quantity of soap is formed to emulsify the fats.

The investigation covered also the action of the lime-boil on mineral and vegetable oil stains, the saponification of fatty bodies by ammonia soda, caustic soda, and various mixtures of the two. With the lime-boil at 120°, the natural fats of cotton are saponified in less than two hours, and tallow in four hours.

From the results of his experiments, Scheurer gives as practical processes for the removal of fatty matters from cotton:—

1. A single boil with caustic soda and resin soap, preferably in the Mather & Platt kier.

2. A lime-boil, followed by a sour and a soda-ash lye-boil, this second process, from its reliability and adaptability, not being likely to become obsolete.

Cotton mordanted with various metallic mordants was also submitted to the various operations of the bleaching process. The mordants chosen for the purpose were pyrolignite of iron, ferric acetate, and the acetates of alumina, lead, tin, and magnesia. Boiled with lime under pressure, the magnesia was completely removed from the cloth, and only a trace of lead was left, but the FeO, Fe_2O_3, SnO_2, and Al_2O_3 had more or less resisted this treatment. The amount of mordant retained was least in the case of bleached cotton, greater with bleached cotton prepared with Turkey-red oil and with unbleached, and greatest with bleached cotton oiled by the old Turkey-red process. Souring removed all the oxides except SnO_2.

By boiling with soda ash under pressure, all mordants were removed except iron.

Ambühl* gives the following figures for a sample of cotton yarn which he had examined (1) in the grey, (2) after boiling in the kier, and (3) after being thoroughly well bleached:—

	Free Fat. Per cent.	Fatty Acids. Per cent.	Ash. Per cent.
Grey,	1·0448	0·1359	1·6294
After boiling with caustic and ash,	0·1761	0·0923	0·2230
Bleached,	0·0210	0·0433	0·0571

The manner in which the hypochlorites act in bleaching proper is a subject which has not received that amount of attention which its importance would warrant, not so much from the point of view of economy† as from that of maximum efficiency, combined with the minimum of deleterious action on the fibre. The usual explanation of the bleaching action of chloride of lime is to the effect that the calcium hypochlorite readily parts with its oxygen—

$$Ca(OCl)_2 = CaCl_2 + O + O,$$

which in the nascent state attacks and destroys the colouring matter of the

* *Journ. Soc. Dyers and Col.*, 1903, p. 256.

† The average amount of bleaching powder required for obtaining a full white on cotton is about 1 per cent., which incurs a cost to the bleacher of less than 7s. per ton, an amount which, when compared with 7s. per ton in steam alone for each lye-boil, is insignificant.

fibre by oxidation, while leaving the fibre itself intact. This explanation is, however, not quite correct, for in no case does the hypochlorite attack the colouring matter only,* simultaneous oxidation of the fibre substance taking place to an extent which is in accordance with the degree of alkalinity of the bleaching liquor. Since ordinary bleaching powder contains free lime, cotton steeped in its solution, without exposure to the air, is bleached but slowly, and is invariably attacked to a greater or less extent by the time it is bleached. Cross & Bevan found the same to be the case with hypochlorite of soda, which, by successive additions of caustic soda, was found to become less and less efficient as a bleaching agent, and at the same time to attack the fibre more and more as the alkalinity increased. For this reason, hypochlorite of soda, prepared by double decomposition from bleaching powder and soda ash, and naturally containing varying amounts of caustic soda, has frequently been wrongly condemned as an inefficient bleaching agent.

Free hypochlorous acid, on the other hand, is not only more rapid in its action than its salts, but is also far less prone to attack the fibre. It is not certain how far back the custom of many bleachers dates, to expose the goods after impregnation with bleaching liquor to the air, but it is likely that the beneficial action of this treatment was recognised, at least by some, soon after bleaching powder was placed on the market. During the exposure of the goods containing the bleach solution, the carbonic acid of the air neutralises, in the first instance, the free lime and then attacks the hypochlorite, liberating free hypochlorous acid :—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O,$$
$$Ca(OCl)_2 + CO_2 + H_2O = 2HOCl + CaCO_3,$$

which, being unstable, gives up its oxygen :—

$$HOCl = HCl + O.$$

Similar changes take place when yarn or pieces are bleached in the cistern at the moment when the bleach solution is being showered over the goods.

Various processes have been patented with the object of imitating this process by artificial means. Of these mention may be made of the processes of Mather-Thomson, Lunge, and Sumner & Hadfield, which are described further on, and the practice adopted by Thies of adding to the bleaching liquor a sufficiency of sulphuric acid to liberate a portion of the hypochlorous acid. The addition of acetic or formic acid for the purpose would be safer, though more expensive.

It is a remarkable fact that the base with which the hypochlorous acid is combined also plays an important part in the efficiency of hypochlorites as bleaching agents. Thus, sodium hypochlorite bleaches much better than potassium hypochlorite, and is in its action about equal to bleaching powder, while lithium hypochlorite bleaches better than any. The influence of soluble chlorides in the bleaching bath is of greater practical importance. Thus, it was found by Knecht that the addition of common salt to a solution of hypochlorite of soda (made by double decomposition from bleaching powder and soda) vastly increased its bleaching efficiency. The same was found to apply to the addition of calcium chloride to a solution of bleaching powder. The observation appears to be borne out by the experience of some practical bleachers who use the system of chemicking in the cistern, and who maintain that, if the spent liquor in the well is made up to the required volume with fresh bleaching-powder solution at $1\frac{1}{2}°$ to $2°$ Tw., a better bleach results than if the old liquor is run off and replaced entirely by fresh of the same specific gravity (but containing, of course, a much larger amount of available chlorine).

* No quantitative estimation of the amount of colouring matter in cotton has hitherto been carried out, but it is probably present only in small quantity.

OTHER BLEACHING PROCESSES.

Within the last twenty-five years several other processes have been proposed which differ more or less from the older processes in principle. Some of these have been carried out on the large scale with more or less success. In most of the modern processes, the lime (which, though effective, and for some purposes indispensable) being very liable to give rise to defects, has been replaced by caustic soda. This change has necessitated alterations and improvements in the kiers in order to bring about a more rapid circulation and better means of excluding the air. In many of the processes a treatment with acid precedes the bowking. Undoubtedly the most important, and the one which has met with the greatest commercial success, is that devised by Horace Koechlin and carried into practice in the steamer kier specially constructed for the purpose by Messrs. Mather & Platt.

In this system the lime-boil is entirely dispensed with, and this, as well as the two lye-boils of the old process, is replaced by a single lye-boil in caustic soda and resin soap. The kier in which the lye-boil is effected is shown in section and longitudinal section in Figs. 28 and 29. It consists of a large

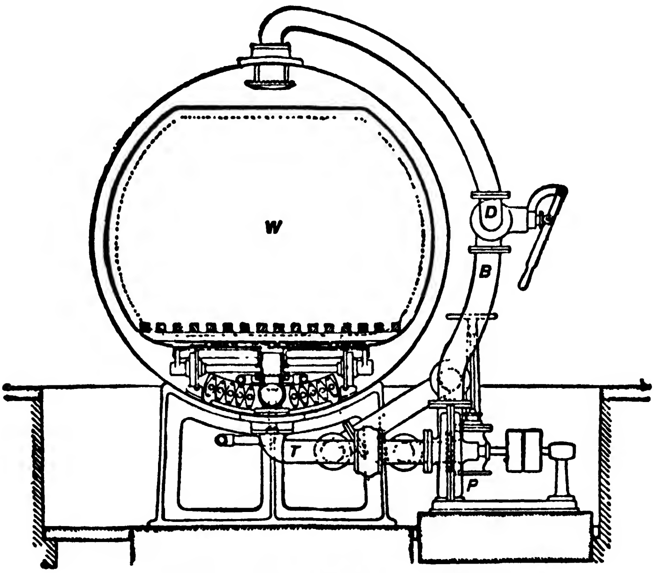


Fig. 28.—The Mather kier. Section.

wrought-iron horizontal egg-ended cylinder, provided at one end with a lid or door. When lowered, the wedge-shaped door fits into a frame, wedging itself steam-tight. The raising or lowering of the door was formerly done by means of a hydraulic ram, but is effected in kiers of more modern construction by a wheel-and-axle arrangement, as shown in the figure.

The goods are packed evenly in waggons, which are made of sheet iron and provided with false bottoms, and which are usually so constructed that two fit into a kier.

The waggons having been run in, the kier is closed, the air expelled by the admission of steam, and a solution of caustic soda caused to shower over each waggon by means of the centrifugal pump, P, through the pipe, B, which divides at D. After percolating through the goods, the liquor collects beneath

the false bottom of each waggon and is drawn thence through the pipe, T, through the centrifugal pump again, a continuous circulation thus being brought about. The circulating liquor in the kier is heated by a coil pipe laid in the bottom, the condense water from which is drawn off outside so as not to dilute the liquor. There is also a perforated pipe to boil by direct steam, if necessary.

When the waggons have been run out, fresh ones are ready to take their place, and thus a great saving in time is effected.

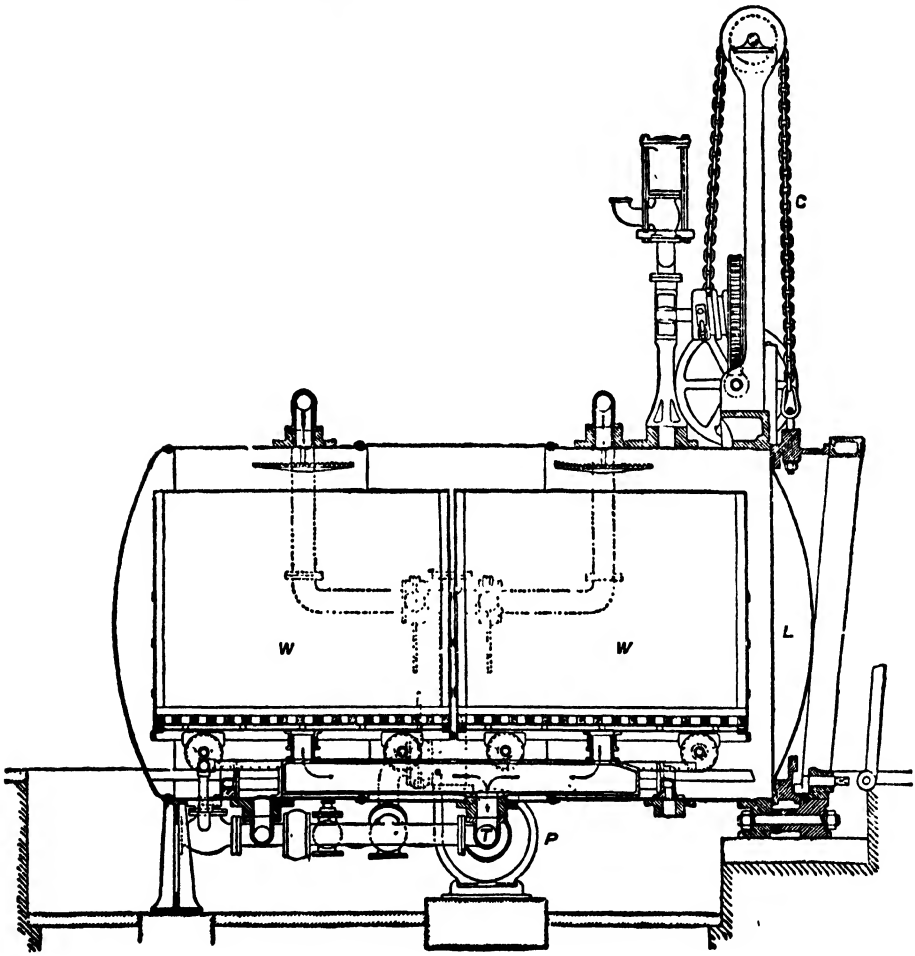


Fig. 29.—The Mather kier. Longitudinal section.

The chemicking, souring, washing, &c., which follow the treatment in the steamer kier may be carried out as in the ordinary bleaching process.

The kier may also serve for boiling with lime, and is sometimes used for this purpose in bleaching "back greys" which have been used in calico printing.

The time required for a full bleach by this method is twenty-six hours. The largest kier made is capable of holding 3·3 tons of cloth, and is capable of turning out regularly 30 tons of bleached calico per week. The main

advantages of the kier are a saving in water, power, time, labour, and fuel, while at the same time the number of operations is reduced, and with these, the wear and tear to which the pieces are otherwise subjected in the bleach-house are reduced.

According to a private communication from M. H. Koechlin, the following is the *modus operandi* employed in the works at Loerrach :—

The grey pieces are passed through sulphuric acid at 2° to 8° Tw., and left in the acid ten to twelve hours, after which they are washed and passed at 75° C. through a bath made up of

1,800 litres water,
25 kilos. caustic soda, 72 per cent.,
5 litres bisulphite of soda, 64° Tw.,

for every 250 pieces of 100 metres each. They are then packed evenly in the waggons and run into the kier. Here they are treated for eight hours (under 7 to 15 lbs. pressure) with a solution of

2,000 litres water,
30 kilos. caustic soda,
40 ,, soda ash,
20 ,, resin.

Wash in kier four to five times with cold water. Then circulate a solution of bleaching powder made up from

2,000 litres water,
100 ,, chloride of lime solution at 12° Tw.,
2 ,, hydrochloric acid.

Allow to circulate five hours. Wash in kier, pass through sulphuric acid at 2° to 8° Tw., wash in washing machine, and dry.

According to another system proposed by *Messrs. Grether & Bentz*, for which a machine has been constructed by Messrs. Edmeston & Sons of Manchester, the operation of boiling with alkali is rendered continuous.* The machine constructed for this purpose consists of a rectangular iron tank provided at each end with a partition which reaches nearly to the bottom. These partitions dip beneath the surface of the liquid and act as water seals for the interior air-tight compartment.

The working of the kier will be readily seen from the figure (Fig. 30), in which part of the side is removed in order to show the internal arrangement of the rollers. The pieces pass in underneath the first partition (either at full breadth or in rope form) and over a number of rollers through the boiling alkali, thus traversing the upper part of the kier several times horizontally, and ultimately passing out beneath the second partition or water seal. They are thus subjected to the action of the boiling alkali and soap in the lower part, and to the action of steam under a slight pressure in the upper part of the kier. The pressure in the interior will depend upon the difference in height of the levels of the liquid on either side of the partitions. The pieces pass through at the rate of about 30 yards per minute.

The time taken for the goods to pass through the kier is so short (under two minutes) that the action of the alkali is by no means complete. On emerging from the kier they are consequently piled up in wooden boxes and allowed to lie with the hot liquor in them for four to five hours. The action of the alkali is thus considerably prolonged. After being washed off, the pieces are chemicked and soured in the ordinary way.

Messrs. Rigamonti and Tagliani have patented † a form of continuous kier which is a modification of the Grether-Bentz kier, differing from the latter,

* *The Dyer and Calico Printer*, February, 1891.
† *Journ. Soc. Dyers and Col.*, 1901, p. 232.

however, in that the cloth enters into and leaves the kier through one and the same column of liquid. Furthermore, a considerable accumulation of cloth takes place in the kier, and, on entering, boiling lye is spurted on to the pieces. The working of the kier will be readily seen from the figure (Fig. 31).

The pieces enter at *i*, passing in a downward direction under the seal into the body of the kier, where they are plaited into the U-shaped receptacle in the middle, and whence they are drawn by means of the tension rollers, *j j*, and pass across the top of the kier, then down to the bottom and out through the seal, being squeezed before leaving the apparatus by squeezing rollers, *r*. The liquor is introduced into the kier by means of a steam injector through perforated pipes, *p*, the lye being kept continuously in motion by means of a pump which conveys it from the bottom of the kier to pipes, *p*. As the impure liquor is continuously passing off through the overflow opening, *s*, a

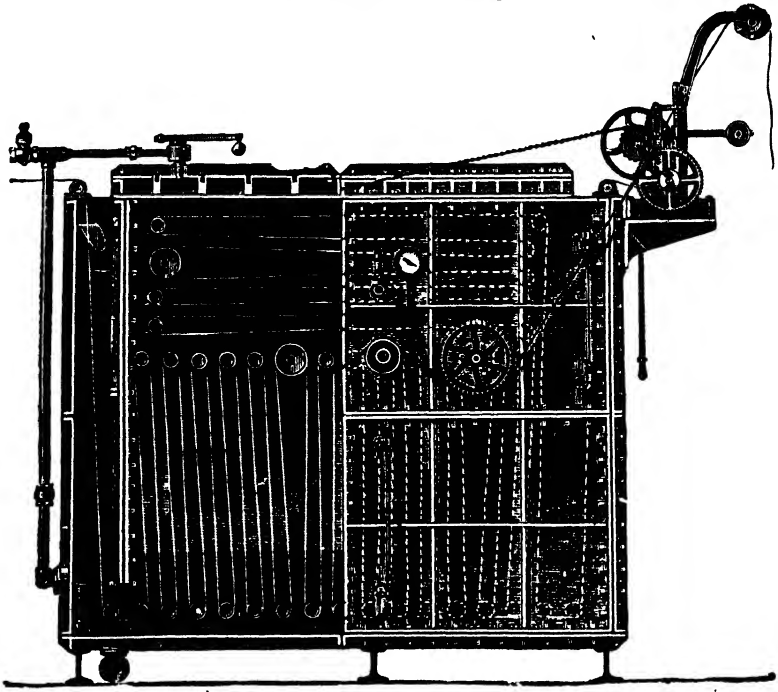


Fig. 30.—Grether & Bentz's bleaching kier.

corresponding quantity of fresh lye is supplied by a pipe connected with the injector.

Bleaching Kier of Muntadas y Rovira.—In this kier, which is intended for open bleaching, the same principle of hydraulic seals is adopted as in the Edmeston-Bentz kier, but instead of there being one compartment with a seal at each end, there are several. The pressure in each successive compartment is thus multiplied until the middle compartment is reached, and then diminishes in like manner towards the exit. It is clear that if the difference in the heights of the columns outside and inside the first compartment corresponds to, say, 5 lbs. pressure (about 10 feet), the pressure in compartment ii. will be double that of the first, since, in addition to the column of liquid which the steam pressure has to raise in i., it has to raise a similar column in ii., so that in compartment iv. there will be a pressure of 4 × 5 = 20 lbs. The construction of the

water seals which follow is the converse of that of the caustic seals, and the pressure will consequently drop by 5 lbs. in each successive compartment until the goods emerge. An important feature of this kier is the adoption of the counter current principle, both in the case of the kier liquor and the wash water. The caustic liquor passes successively from compartment iv. to compartment i. and overflows at the top of the first seal. The principle on which this kier is constructed is excellent, from a theoretical point of view, but, as in the case of the Edmeston-Bentz kier, it is not practicable to allow the goods to pass through sufficiently slowly to allow of an efficient "bottoming."

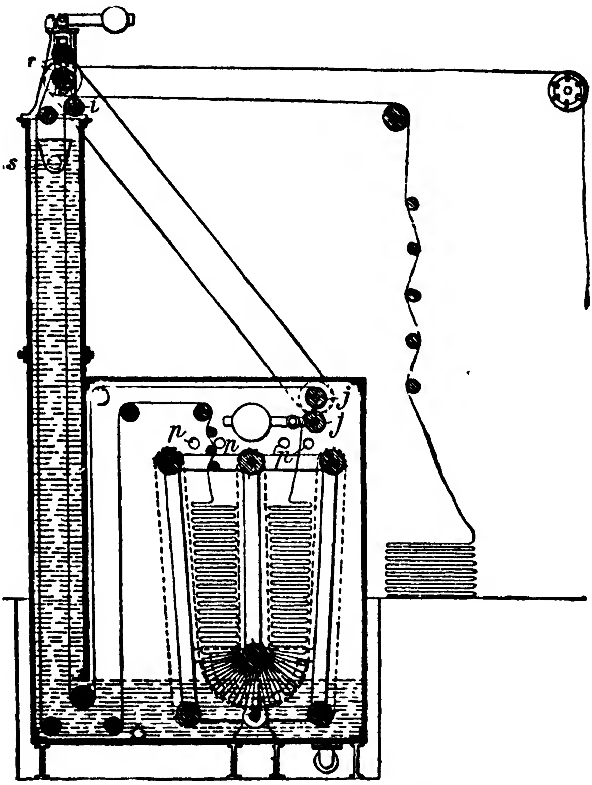


Fig. 31.—Rigamonti and Tagliani's kier.

The Mather-Thompson Continuous Bleaching Apparatus was devised with the object of effecting the further treatment of the goods after they have been boiled with caustic soda in the Mather kier. It contains 15 partitions in which the chemicking, treatment with carbonic acid, washing, and souring are effected. In the first partition the pieces are simply run through warm water; in the second they pass through chloride of lime at 2° Tw. The third partition is a chamber filled with carbonic acid gas, the pieces passing in and out through narrow slits. In the fourth, fifth, and sixth partitions they are washed with cold water; in the seventh they pass through a soda solution (1 grm. per litre) at 60° to 75° C.; in the eighth, ninth, and tenth they are washed again with water. In the eleventh partition they are again passed through chloride of lime, this time at ½° Tw. The twelfth is a second carbonic acid chamber, and the thirteenth, fourteenth, and fifteenth contain weak hydro-

chloric acid (1 per cent. solution). After leaving the apparatus the goods are washed in an ordinary washing machine, and dried.

The speciality in the Mather-Thompson process is the use of carbonic acid after the chloride of lime, the effect of which is, as has been pointed out before in the description of the ordinary bleaching process, to liberate the free hypochlorous acid on the fibre, and thus accelerate the bleaching action.

Bleaching Process of Thies and Herzig.—The following are the main features of this process:—The goods are first run through (hot) very dilute acid, steamed for a short period, and washed. The bowking is effected with caustic soda (of greater strength than usual) and resin soap in a specially constructed kier, in which the circulating lye is heated by indirect steam and the bleaching proper by means of hypochlorite of soda in place of bleaching powder. The process was the outcome of an extensive and carefully conducted research which was carried out by Messrs. Thies and Herzig, and, although this was done over twenty years ago, it will not be out of place to mention here some of the experiments, for an account of which we are indebted to Mr. H. Thies.

The first experiments were done with cotton pieces in Barlow kiers with the object of ascertaining the effect of the oxygen * contained in the steam on goods in the ordinary condition, and such as had been limed. The result was that after 45 minutes steaming the goods containing no lime had comparatively little effect on the amount of oxygen present; the limed goods, similarly treated, had absorbed almost every trace. Nevertheless, the latter were not tendered. By employing caustic soda of a strength equivalent to that of the lime water no diminution of the amount of oxygen was noticed. But on increasing the amount of caustic fivefold it was found that the oxygen had all been absorbed, and the goods surrounding the central pipe of the kier were browned and tendered. It is evident from this that lime and caustic soda act differently. The lime acts more slowly, and any formation of oxycellulose will be evenly distributed in the goods throughout the kier, while the caustic soda acts rapidly with consequent excessive formation of oxycellulose at the places where the steam enters. It was furthermore ascertained that, in the case of lime, the oxygen acts more on the impurities than on the cotton, and, being consumed in this way, the fibre is left intact.

Further experiments, in which fents of cotton dyed with indigo were placed among the goods in the kier, showed that in time the kier liquor acquires a reducing action, the indigo fents being decolourised at some distance from the central pipe, both in the case of lime and of caustic soda. It is consequently advantageous to pass the goods, previous to their being packed in the kier, through the kier liquor from a previous operation.

The following is a description of the process as at present carried out:—

The goods run straight from the singeing machine, or, after having been simply wetted-out with water, through very dilute acid (16 grms. hydrochloric acid (30 per cent.), or 10 grms. sulphuric acid (60 per cent.), along with ½ grm. hydrofluoric acid (75 per cent.) per litre), and are steamed for 20 to 60 seconds. The effect of this treatment is to render soluble the whole of the starch contained in the size by converting it partially into soluble starch and partially into dextrine. By the action of the hydrofluoric acid, compounds of iron, alumina, and silica are removed. After souring, the goods are first run through a bath containing kier liquor from a previous operation, then through a weak solution of magnesium chloride (50 grms. per litre), after which they are squeezed and packed in the kier.

* Water always contains some air in solution, most of which is expelled on boiling. The steam used in these particular experiments contained 16·4 to 18·5 c.c. air per kilo., and of this 22 to 23 per cent. was oxygen.

The construction of the Walsh kier, which is the same in principle as that of the original Thies-Herzig kier is such that no steam can come into direct contact with the kier liquor, and formation of oxycellulose, due to the air expelled from the water in the boiler, is thus entirely avoided. To this end, the heating of the kier liquor is effected by means of a steam kettle adjacent to the kier, and the circulation of the liquor is brought about by means of a centrifugal pump. The arrangement is shown in Fig. 32, in which K

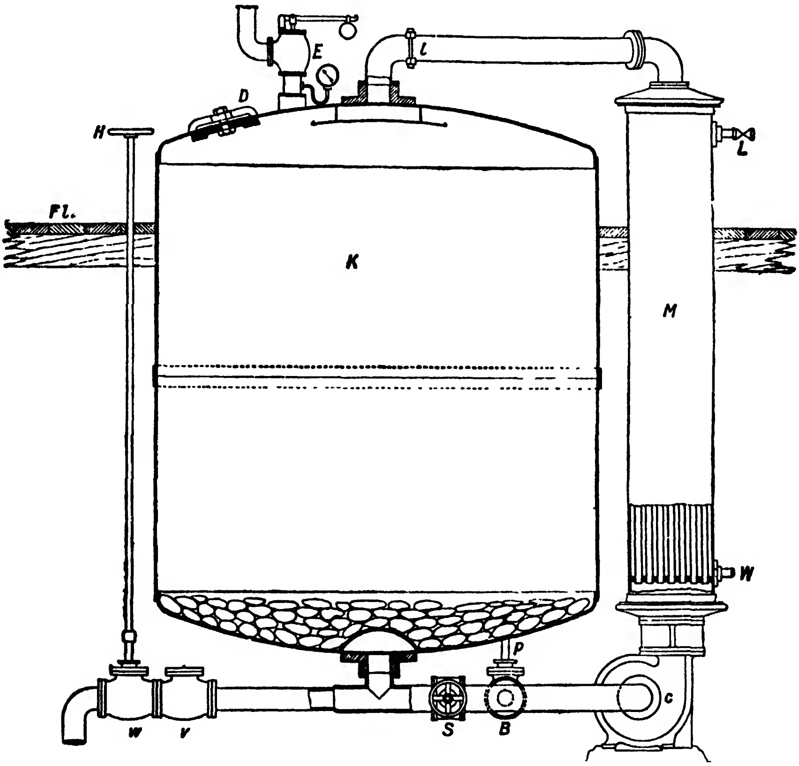


Fig. 32.—Walsh kier.

represents the body of the kier with rounded stones acting as a false bottom; H the hand-wheel actuating the let-off (waste) valve, *w*; *v* the back-pressure valve; B the water supply with spindle, *p*, to water valve; S the sluice valve; C the centrifugal pump connecting the outlet from the bottom of the kier through S, with upright multitubular heater, M, heated by steam through valve, L, the condense water issuing at the lower extremity at W; D is the manhole; E the safety valve; while Fl represents the floor line.

In the Thies-Herzig kier, a cylindrical recess is rivetted to the bottom in order to provide a larger space for the collection of the percolating liquors.

The goods having been packed into the kier, the air is first displaced by blowing steam in, and caustic soda of 9° to 12° Tw., which has previously been boiled to expel the air and which contains in solution 7½ kilos. resin for every ton of goods, is circulated under pressure. The goods are then washed in the kier, first with hot and then with cold water. The duration of the bowking operation is eight to ten hours.

From the kier, the goods run through one, or in some cases two, washing machines into the bleaching cistern in which a faintly acid solution of hypochlorite of soda * is circulated through them for four hours. The amount of chlorine (calculated as bleaching powder) required for effecting a complete bleach by this process is said not to exceed 0·2 per cent. of the weight of the goods. The acidulation of the bleaching liquor serves to prevent the goods becoming yellow on storing.

After bleaching, the goods are passed through a weak boiling solution of soda, after which they are again steamed, washed, and dried.

In the improved kier of Thies, a vacuum boiler (an upright cylindrical vessel, similar in size and shape to an ordinary kier) is inserted between the kier and the superheater, the capacities of the two vessels (for an ordinary sized plant) being 14 and 15 cubic metres respectively, while the centrifugal pump is replaced by a Grindle pump, which is more efficient in its action. The bowking takes place in two stages—viz., a preliminary one of two hour's duration, in which liquor from the previous operation is used, and the bowking proper, with fresh caustic soda and resin soap, which lasts six hours.

The goods saturated with alkali (liquor blown off from the previous preliminary bowking, see below) are packed into the kier, and then, by means of the Grindle pump, the old kier liquor is drawn from the vacuum boiler (which is quite full to start with, and closed at the top), and sent in at the bottom of the kier until the latter is quite full, the air escaping through a blow-off valve at the top. As soon as the kier is full, the air valve is closed. By pumping the liquor from the vacuum boiler into the kier, a vacuum equal to about 10 lbs. is produced in the former vessel. A pipe provided with a throttle valve connects the top of the kier with the top of the vacuum boiler. This valve is now slightly opened, so that a circulation of the liquor takes place, while any air contained in the kier rises with the liquor, passes through the throttle valve into the vacuum boiler, where the liquor falls to the bottom and the air expands into the vacuum. The pressure in the kier is now gradually increased to 3 atmospheres by choking the valve, when any air remaining in the goods is mechanically dissolved (air being more soluble in water under pressure) out of the goods, and transferred to the vacuum boiler. After the air in the vacuum boiler has been expelled, steam is turned on in the superheater, and the bowking continued for two hours at 45 lbs. pressure. The pump is now stopped, the steam turned off, and the liquor blown off under its own pressure. Fresh lye, consisting of caustic soda at 6° to 7½° Tw. and resin soap, is now run into the kier (which is free from air), the pump set in motion again, steam turned on in the superheater, and the bowking proper continued for six hours at 45 lbs. pressure.

The further treatment of the goods is the same as in the old process.

Open Bleaching.—The simplest (though not by any means the most economical) method of bleaching cotton piece goods in the open state is to conduct the operations of boiling in alkali, chemicking, and washing on the jigger (*q.v.*), and this is largely done in small dye-works. The operations and materials used are practically the same as in the ordinary caustic soda bleach,

* The hypochlorite of soda is prepared, according to Thies and Herzig, as follows:—290 kilos. bleaching powder of 33 per cent. are ground to a paste with 1,100 litres water, and to this are added 175 kilos. ammonia soda dissolved in 500 litres water, along with a sufficiency of water to make up to 2,000 litres. After stirring for half an hour, the mixture is allowed to stand overnight, when the clear liquor is decanted. The sediment is mixed with fresh water, the clear liquor being again decanted, and this process repeated until in all 5,000 litres of liquor (of 6° to 6½° Tw.) are obtained. The solution, which is alkaline, is said to keep for a long time. In order to liberate 10 per cent. of the hypochlorous acid, about 6 to 7 grms. sulphuric acid of 60° B. are added to every litre of the bleaching liquor.

and the method does not call for any special comment. Very good results are obtained in this way.

For the more economical treatment of large quantities of goods (*e.g.*, velveteens) in the open state, the boiling is usually effected in large rectangular open kiers constructed of iron, in which the goods are plaited down in such a manner as to avoid any creasing. The rest of the operations may either be carried out on jiggers, or by running the goods at full width through vessels provided top and bottom with guide rollers.

Jackson and Hunt's Open Bleaching Kier.—In a sense this is similar to bleaching on the jigger, but differs from this simple process, inasmuch as the operation of boiling is conducted under pressure. The goods are first batched in a specially constructed machine, which is shown in section in Fig. 33. This consists of a cast-iron cistern in which a large perforated drum is mounted on

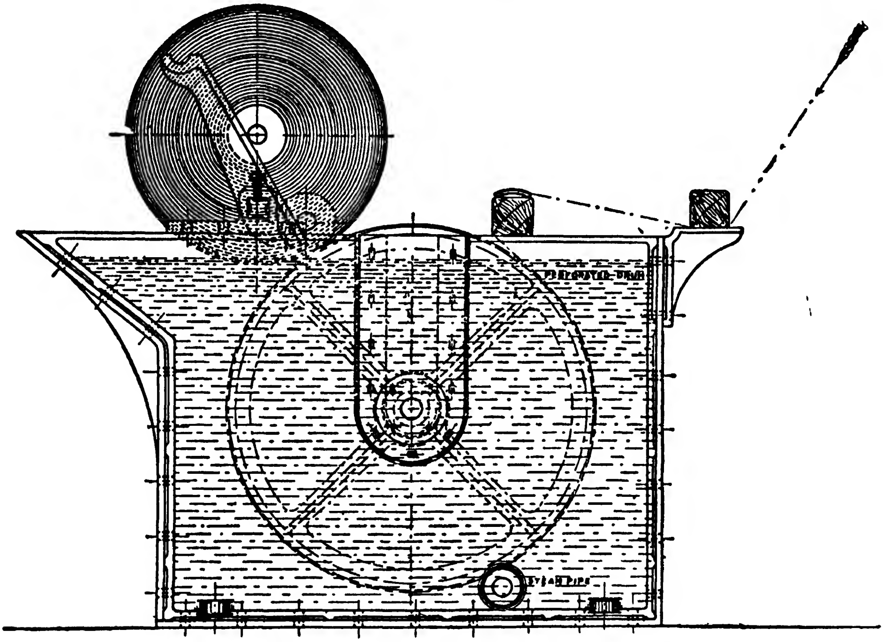


Fig. 33.—Batching machine for Jackson-Hunt kier.

bearings. The cistern is filled with caustic liquor (which has already been used in the kier), and the cloth, which is indicated by a dotted line, passes round the drum and becomes thoroughly saturated. In close proximity of the drum, and near the bottom of the cistern, is a perforated steam pipe, which serves for heating the liquor and driving it through the cloth as it travels with the drum. On leaving the cistern the goods are batched on the roller, which rests with its own weight on the drum, and is kept in position by a pair of strong batch arms, which are fixed on the top of the cistern. Each batch contains from 1,900 to 2,200 yards of cloth. When the batch roller has been filled in this way, it is placed in position on a waggon in juxtaposition to an empty batch roller, and the waggon is run into a horizontal high-pressure kier, in which the rollers automatically couple with driving gear at the back, by which means the pieces are wound off one batch roller on to the other, and *vice versâ.* Resting on the batch rollers with its own weight is a heavy

perforated drum. The door of the kier having been closed, caustic soda liquor is run in by means of a centrifugal pump, steam is turned on until a pressure of 40 lbs. is reached, and the cloth is wound off one batch roller on to the other and *vice versâ* for two hours, the boiling caustic liquor being in the meantime circulated and showered on to the goods from the top of the kier.

Chemicking, souring, and washing are effected in machines which work on exactly the same principle as the kier as regards the running of the cloth, and this is explained by reference to Fig. 34, which represents the kier in cross-section. The two batch rollers (each represented as being partly filled with cloth), A and B, work in journals carried by the framework, F. S represents the shell of the kier, while the perforated drum, C, carried by oscillating arms, which are free to move from side to side, is journalled at F. The arms having an open jaw at the top, the drum adjusts itself to the increasing

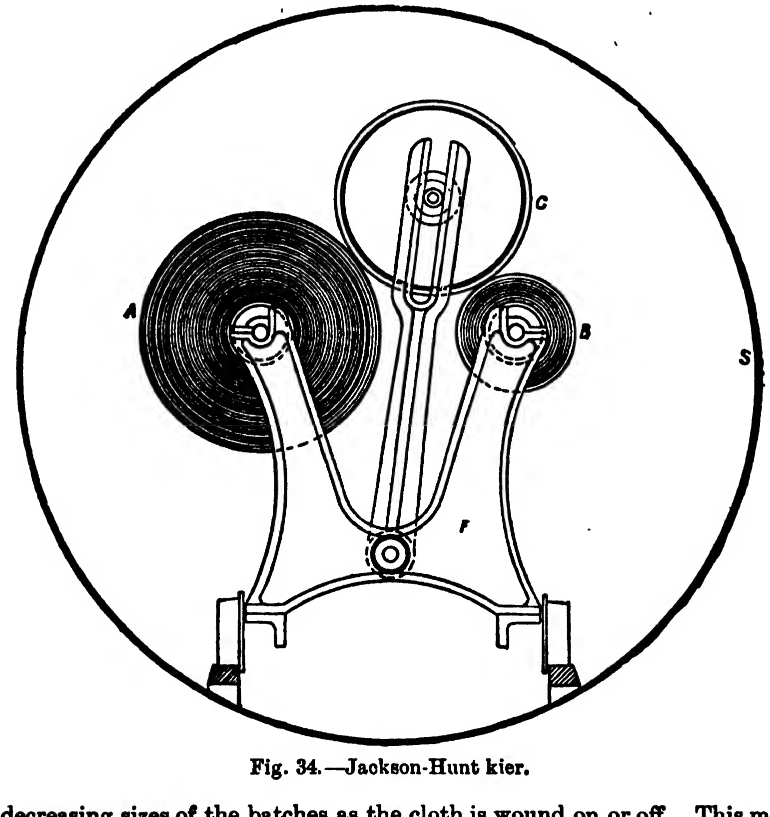


Fig. 34.—Jackson-Hunt kier.

and decreasing sizes of the batches as the cloth is wound on or off. This motion is important, as it keeps the cloth always at the same tension and absolutely free from creases. It also brings considerable pressure to bear on the rotating batches, and thus squeezes the liquor through the cloth, while, lastly, it prevents either entirely or to a large extent curly selvedges. The washing, &c., of the pieces is effected by means of an arrangement similar to that shown in the kier.

Lunge's Improvements in Bleaching consist in the use of acetic acid along with the bleaching powder. Free hypochlorous acid is thus liberated, according to the equation—

$$2CaOCl_2 + 2C_2H_4O_2 = CaCl_2 + Ca(C_2H_3O_2)_2 + 2HOCl$$

The free hypochlorous acid, in acting on the constituents of the cotton, gives up its oxygen; and free hydrochloric acid results—

$$2HOCl = 2HCl + O_2.$$

The free hydrochloric acid resulting from this decomposition is just sufficient to liberate the acetic acid again from the calcium acetate formed in the first instance—

$$Ca(C_2H_3O_2)_2 + 2HCl = CaCl_2 + 2C_2H_4O_2.$$

The process thus becomes continuous, and a given amount of acetic acid suffices to decompose a very large quantity of bleaching powder. The subsequent treatment with acid is rendered unnecessary and the expense and time of one operation are thus saved. In place of acetic acid, formic acid can be used.

In the process patented by Hadfield, Sumner & Hadfield,* the goods after having been boiled in the kier, and washed, are run through bleaching powder and then through a chamber containing acetic acid vapour which is generated by allowing acetic acid to drop on to a steam-heated plate. The action of the acetic acid is the same in this case as in Lunge's process, but the acid is not regenerated.

Bleaching by means of Electrolytically prepared Hypochlorite Solutions.—When a solution of common salt is electrolysed, the electro-negative chlorine ions migrate towards the positive electrode (or anode), while at the electro-negative electrode (or cathode) there is a corresponding accumulation of the electro-positive sodium ions. The sodium which collects at the cathode instantly reacts, however, with the water, forming caustic soda and hydrogen gas, which latter, being practically insoluble in water and very light, escapes as such. The chlorine, on the other hand, collects at the anode. If the electrolysis is conducted in a cell provided with a porous diaphragm, a more or less complete separation of the caustic soda and chlorine may be effected, the former being concentrated and obtained in the solid state, while the latter is usually absorbed in lime to form bleaching powder. Considerable quantities of these electrolytically prepared products are being used at the present time.

If, on the other hand, the electrolysis of the salt solution is effected without a diaphragm and the electrodes are placed in close proximity to each other, the chlorine does not escape, but reacts at once with the caustic soda formed at the cathode producing sodium hypochlorite † and sodium chloride—

$$2NaOH + Cl_2 = NaOCl + NaCl + H_2O.$$

Various forms of apparatus have been constructed by Hermite, Kellner, Vogelsang, Haas and Oettel, and others, for the electrolytic production of bleach solutions by means of this reaction. The bleacher is thereby enabled to dispense with the use of bleaching powder, using in its place a solution of common salt (brine), which is rendered effective by being simply passed through the electrolyser. A clear solution of hypochlorite is thus obtained, which does the work of bleaching powder or of hypochlorite of soda (prepared from bleaching powder by double decomposition) equally well. When brine or salt can be obtained cheap, and cheap water or steam power is available, these electrolysers will no doubt be found useful, but under ordinary conditions of working their adoption by bleachers is not likely to make much headway, chiefly because they do not offer any advantage as far as cost of production is concerned as compared with the old-fashioned bleaching powder—cost of plant, wear and tear of electrodes, cost of power, and loss of unchanged sodium chloride being all

* English Patent No. 29,645, 1896.

† It is essential that during the process the temperature should not be allowed to rise much, otherwise the reaction would take place in a different sense, and chlorate of soda (which is of no value as a bleaching agent) would result in place of hypochlorite.

contributory factors which militate against the success of the electrolytic method. Theoretically, the loss of salt could, of course, be reduced to a minimum by electrolysing the spent bath over again, but the impurities which the latter takes up from the goods in bleaching require so much power (fresh hypochlorite not being formed until these are destroyed) that this is out of the question from a practical point of view.

It has been asserted that the electrolytically-prepared hypochlorite solutions are far more effective in bleaching than solutions of equal chlorine strength prepared by purely chemical means,* and it has even been asserted that this difference may amount to as much as threefold in favour of the electrolysed brine. Such assertions cannot, however, be taken seriously, and the special virtues which are ascribed to the action of electricity on chlorine are probably purely imaginary ones. For, although it may be shown experimentally that electrolysed brine bleaches more rapidly than hypochlorite of soda prepared from bleaching powder, this difference may partly be accounted for by the fact that the electrolytic bath is neutral, while the hypochlorite of soda is alkaline; and, further, according to Knecht, by the presence in the former of a large excess of undecomposed sodium chloride. By adding sodium chloride to the ordinary hypochlorite of soda, its bleaching action is greatly enhanced.

BLEACHING WITHOUT CHLORINE.

The use of chlorine for cotton bleaching is not altogether indispensable. Cotton freed from the natural impurities soluble in alkalies and acids is bleached if exposed to light for a sufficient length of time. However, this process, although used to some extent in linen bleaching, is seldom adopted for cotton, as it takes too long, and would not be suitable for dealing continuously with large quantities.

Bleaching with Peroxide of Hydrogen.—This bleaching agent would, no doubt, rapidly supersede chloride of lime in the bleaching of calico if its price were to come down sufficiently low, since it produces a better white, and there is no risk of tendering the fibre. The best results are obtained with it by means of the method proposed by Horace Koechlin.

For five pieces of 100 metres each, or about 50 kilos. of cotton, prepare a bath with—

Water,	100 litres.
Caustic soda,	10 kilos.
Soap,	30 ,,
Calcined magnesia,	8 ,,
Peroxide of hydrogen of 12 volumes strength,	50 litres.

Boil the goods in this solution for six hours, wash, pass through sulphuric acid at 3° Tw., and wash again.

If the calcined magnesia is not added to the bath, the decomposition of the peroxide takes place so rapidly that the oxygen generated has not time to take effect. Its action in retarding the evolution of the oxygen is due, according to Prudhomme,† to the formation of a hydrated peroxide of magnesium corresponding to the formula $(3Mg(OH)_2 + MgO_2)$ or $(3Mg(OH)_2 + MgO(OH)_2)$, which decomposes very slowly at the boiling temperature.

The magnesium soap which forms during the boiling is not of a sticky nature, and is easily removed from the pieces by washing in water.

In place of hydrogen peroxide, Königswärter and Ebell recommend the use of sodium peroxide, of which 1 per cent., calculated on the weight of the material, is said to suffice. The bleaching bath should contain besides three

* Saget, *Journ. Soc. Dyers and Col.*, 1896.
† *Journ. Soc. Dyers and Col.*, 1891, p. 136.

times as much magnesium sulphate as of sodium peroxide in order to neutralise the alkali. The bleaching is done at 40° to 45° C., and takes one to three hours.

In some cases it is advisable to bleach first in the ordinary way with bleaching powder and to finish off with hydrogen peroxide. According to Lunge,* hydrogen peroxide serves simultaneously as an antichlor, thus preventing a tendering of the fibre.

Bleaching with Permanganate of Potash.—Permanganate of potash is a powerful oxidising agent, and, as such, is capable of destroying the natural colouring matter of cotton. As in bleaching with chlorine, it is necessary to remove the grease and wax-like impurities by boiling with alkalies previous to bleaching. The method usually recommended is to steep the cotton thus prepared in a slightly acid solution of permanganate of potash. The addition

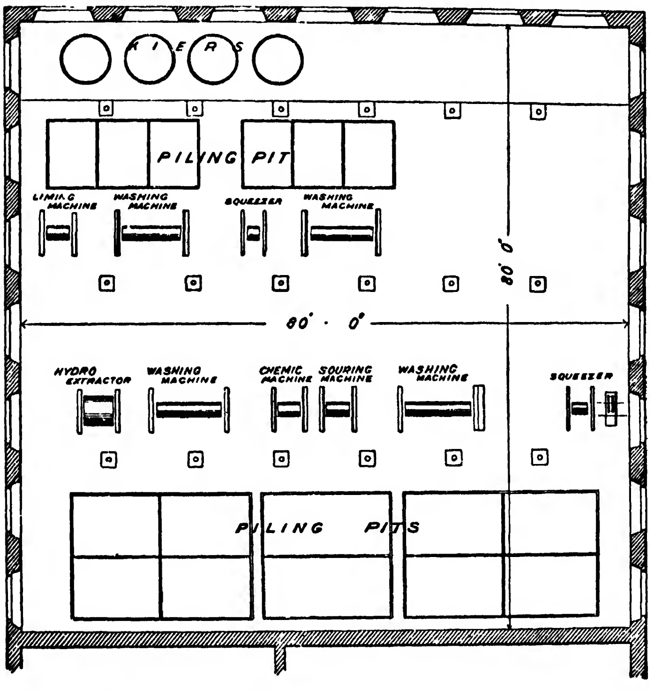


Fig. 35.—Plan of bleach-house with ordinary kiers.

of acid, or, better still, of magnesium sulphate, to the permanganate, is necessary to prevent the bath becoming alkaline, with consequent formation of oxycellulose. In giving up part of its available oxygen, the permanganate yields caustic potash—

$$2KMnO_4 + 3H_2O = 2KOH + 2MnO(OH)_2 + 3O.$$

When taken out, the cotton is of a more or less dark brown colour, due to the reduction of the permanganate and the consequent deposition of peroxide of manganese on the fibre. This can be rapidly and completely removed by passing the cotton through a solution of sulphurous acid or bisulphite of soda.

* *Dingl. Polyt. Journ.*, 1886, p. 196.

By this process, part of the available oxygen originally contained in the permanganate is lost in the peroxide which deposits on the fibre. In order to obtain the complete effect of the available oxygen, Manzoni * has proposed the following method:—

The cotton yarn is freed from grease and wax-like impurities by boiling in a solution of caustic soda (4 grms. per litre) under 2 atmospheres pressure. It is then well washed and steeped for five hours in a solution of sulphuric acid at $7\frac{1}{2}°$ Tw., to which the permanganate is added in concentrated solution in two or three different portions. Under these conditions, the yarn does not turn brown, the acid being strong enough to decompose any peroxide of manganese which might form, according to the equation—

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

The operation being carried out in the cold, no tendering of the fibre takes place; but it is necessary to wash well as soon as the cotton is taken from the

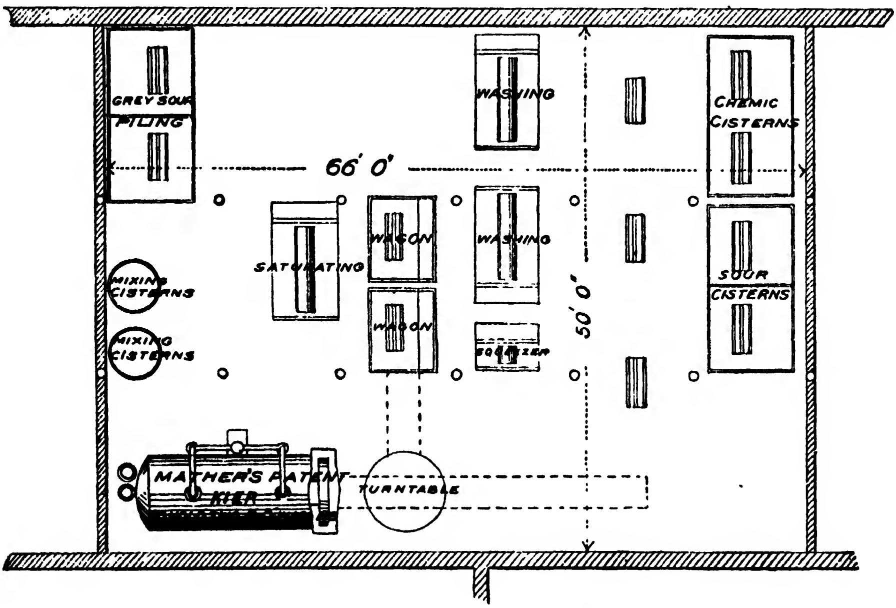


Fig. 36.—Plan of bleach-house with Mather kier.

bleaching bath. Manzoni maintains that, in working by this method, a much smaller amount of permanganate is necessary than in the old process; he finds that half a kilo. of permanganate is sufficient to produce a good ordinary white on 100 kilos. of cotton yarn.

Bleaching with Calcium Sulphite and Caustic Soda.—According to Horace Koechlin, an excellent white may be produced on cotton piece goods by the following simple process:—The pieces are impregnated with a mixture of milk of lime and sulphite of soda (which by double decomposition would form calcium sulphite and caustic soda), steamed for one hour, washed, passed through acid, and washed again.

A similar process has been advocated by Saget.†

* *Journ. Soc. Dyers and Col.*, 1889, p. 98. † *Ibid.*, 1901, p. 123.

FAULTS IN BLEACHED COTTON.

Although the bleaching of cotton is apparently a straightforward and comparatively simple process, the occurrence of faults or defects in the bleached material is by no means uncommon. Defective bleaching is not always apparent in the bleached goods, and may only show itself after storing for some time or after washing, or, again, in dyeing the goods in light shades or in the process of finishing. Thus, cotton which has been imperfectly "bottomed" can be bleached white by means of bleaching powder, but is liable to turn yellow on storing. In order to ascertain whether this is likely to occur, Ambühl * recommends the quantitative determination of (1) free fat, which should not exceed 0·04 per cent.; (2) fatty acids, which should not exceed 0·12 per cent.; and (3) ash, which should not exceed 0·5 to 0·6 per cent.

Imperfect bleaching is often hidden by excessive blueing of the goods. When the blue is washed out, the defect is at once apparent. It sometimes happens also that the blue is destroyed locally by light or chemical action, and the goods thus assume a spotted or uneven appearance.

Defects in bleaching may only reveal themselves in the subsequent dyeing of the goods, the colours coming out uneven or containing either spots or streaks, especially when direct colours are used. The chief factor in causing a defect of this kind is the local formation of oxycellulose, which may either be due to insufficient exclusion of air from the kier in bowking with lime or caustic soda, or to excessive local action of bleaching powder.† The fault may be detected in the dyed material by stripping the colour—*e.g.*, by means of titanous chloride—and dyeing in a cold dilute solution of Methylene blue. The defective parts (which should be marked in lead pencil previous to stripping) will now dye a darker shade than the rest of the material.

The presence of lime soap in the bleached goods also accounts sometimes for defective dyeing.

Paraffin wax, used without the addition of tallow in the sizing or dressing of the warps, is not removed in any of the operations of the ordinary bleaching process, and frequently gives rise to defective dyeing (acting as a resist to some colouring matters), but more especially in finishing, limp places or patches resulting where the wax is present in any quantity.

Mineral oil, which frequently gets on to the goods from the machinery, and is of a more or less dark colour (from the presence of finely-divided metals or their oxides), is as difficult to remove as paraffin wax. If the spots or other marks are visible after bleaching, the oil may be conveniently removed by sponging with a solvent like ether. Another means of removing either paraffin wax or mineral oil from pieces is to run them through a fairly strong emulsion of olive oil in soda, allow to remain batched for some time, and then soap hot.

Iron mould now and then occurs in bleached goods, and, although it can in many cases be removed by souring in hydrochloric acid, the ferric hydrate is usually dehydrated to such a degree that such a treatment does not suffice. In such cases binoxalate of potash applied locally will frequently be effective, but its action is not infallible. If the iron mould should withstand these treatments, it may be removed either by treatment for some seconds in warm concentrated hydrochloric acid, or with a solution containing a reducing agent, such as copperas and hydrochloric acid. Stannous chloride and oxalic acid, or titanous chloride and oxalate of potash, are still more effective.

* *Journ. Soc. Dyers and Col.*, 1903, p. 256.

† Uneven stretching in the mercerising process (*q.v.*) may also lead to similar faults, cotton mercerised under tension taking up less colour in dyeing than cotton mercerised without, or with only a little, tension.

Iron stains should not be mistaken for peroxide of lead stains, which latter are liable to be formed if the cotton has come into contact with lead or salts of lead previous to being chemicked. These stains, though similar in appearance to iron stains, can readily be distinguished from the latter by the absence of any reaction with an acid solution of yellow prussiate of potash, and by the intense green colouration which they assume when the piece is steeped for a few minutes in a solution of the leucobase of Malachite green in very dilute sulphuric acid.

Tendering of cotton in the yarn or piece is due to two principal causes—viz., formation of oxycellulose (see above) or of hydrocellulose. The latter cause is the most frequent, and is brought about by the action of mineral acids. The fault may occur in several ways, but is generally due to insufficient washing after the final souring in the bleaching process. The goods being afterwards dried, either in stoves or on cylinders, the small amount of acid left in is concentrated on the fibre, and tendering of the fabric results. Tendering may, however, also result from the presence of magnesium chloride in the size—*i.e.*, if the goods are singed before bleaching. During the singeing, the high temperature brings about a hydrolytic dissociation of the magnesium chloride into magnesia and hydrochloric acid, which latter attacks the fibre. The presence of free acid in bleached goods is most readily detected by extracting a small piece with distilled water and adding a drop of Methyl orange, when the occurrence of a pink colour denotes an acid reaction. This indicator is much more suitable for the purpose than litmus. Cotton tendered by acids does not show any increased affinity for Methylene blue.

It is noteworthy that, by mercerising cotton *without* tension after it has been tendered by acid, the original strength may be restored, even if the tendering amounts to 50 per cent.

With cotton piece goods which have been too heavily calendered, tendering may also be due to the crushing or cutting of the fibres.

LINEN BLEACHING.

As has already been pointed out in the description of the fibres, the raw linen fibre contains a much larger amount of foreign substances than cotton. While ordinary raw cotton only contains about 5 per cent. of foreign matter, the loss in weight during the bleaching process amounts, in the case of linen, to some 20 per cent. The nature of the foreign substances (other than cellulose) contained in the raw flax seems to have been but imperfectly studied; it contains a large amount of so-called pectic matters, which can be removed by prolonged treatment with alkalies.

Flax Wax.—The pliability and handle (or feel) of the flax fibre, as well as its characteristic smell, are said to be due to a peculiar fatty substance which adheres to its surface. If, according to C. Hoffmeister,* heckled flax is extracted with any of the usual fat solvents, such as ether, benzine, &c., a more or less greenish-yellow, and slightly fluorescent, coloured solution is obtained, which leaves, on evaporation, a more or less coloured substance possessing an intense smell of flax. The extracted fibre has lost its characteristic smell, most of its pliability, and its lustre, whilst it has acquired a coarse feel and has become almost brittle. The substance thus isolated varies in colour from white to yellowish or greenish-yellow brown, and shows a dull surface on fracture. In the cold it is brittle, but softens when kneaded between the finger and thumb. From a hot saturated benzine solution it separates out on cooling in almost white granules, possessing, apparently, a crystalline structure. Its

* *Journ. Soc. Dyers and Col.*, 1903, p. 182.

specific gravity at 15° was found to be 0·9083, and the melting point 61·5° C. In water it is insoluble, partially so in alcohol, sparingly soluble in chloroform, but readily soluble in other solvents. It burns in the air with a bright smoky flame, leaving no appreciable residue.

The amount of wax contained in different kinds of flax varies considerably, those fibres which have been subjected to the greatest amount of mechanical cleaning containing least wax, while the waste from scutching mills contains considerable quantities (up to 10 per cent.).

Flax wax contains, principally, an unsaponifiable residue (70 to 80 per cent.) similar to ceresin, and consisting of hydrocarbons, ceryl alcohol, and phytosterol. The rest consists chiefly of a mixture of fatty acids, of which palmitic, stearic, oleic, linolic, linolenic, and isolinolenic were identified. In addition, a small amount of an apparently aldehyde-like volatile substance was obtained, which existed, however, in such small amount that it could not be identified.

Linen being more easily affected by alkalies, acids, and chlorine than cotton, the bleaching of linen is, therefore, a longer and more tedious process than the bleaching of cotton. A severe treatment would either result in the tendering of the fibre or in "setting" the colour, and when this latter fault has once shown itself it is difficult to deal with. Another very important point in linen bleaching is the preservation of the lustre of the fibre; if the "skin of the fibre is broken," one of its most valuable properties is lost. The general treatment of linen, either in the yarn or in the piece, is similar to that adopted for cotton; but the reagents are generally weaker, and it is necessary to repeat some of the operations several times before a satisfactory white is obtained.

A special operation necessary in linen bleaching, but not used for cotton, is the "grassing," a remnant of the old method of bleaching which was in use before the introduction of chlorine as a bleaching agent. In grassing, the pieces are exposed in fields, after treatment with alkali and acid, to the joint action of light, air, and moisture. In dry weather the goods are sprinkled with water from time to time. The effect of grassing is considered to be due to the action of the ozone and peroxide of hydrogen which are usually found in small quantities near the ground. Attempts have been made to replace the grassing by a treatment with ozonised air, but have not been successful.

LINEN YARN.

The bleaching of linen yarn is similar in principle to the bleaching of cotton, but the process lasts much longer if a full bleach is required. This is, however, not always necessary. For some purposes a lye-boil and subsequent treatment with acid suffices, while in other cases, the yarn is required quarter-bleached, half-bleached, or three-quarters bleached. As the white increases in purity the strength of the yarn is diminished.

Since linen yarn varies much more in quality than cotton, there is also a considerable variation in the details of the bleaching process. The following may, however, serve as a typical example for a three-quarters white:—

1. *Boil* for eight hours with 10 per cent. soda ash on weight of yarns, wash well, and squeeze.

2. *Reel* for one hour in bleaching powder at $\frac{1}{2}$° to $\frac{3}{4}$° Tw. Wash.

The reeling, which is also a speciality in linen bleaching, is effected in shallow stone, cement, or wooden troughs, of which one is shown in section and three in plan in Figs. 37 and 38.

The reels receive an alternating backward and forward motion from the main shaft. When the operation is over they are removed and replaced by

another lot, freshly filled. During the operation, only a small portion of the yarn lies beneath the surface of the liquid, the rest being exposed to the air, the carbonic acid of which liberates free hypochlorous acid from the bleaching liquor, and thus assists materially in the bleaching.

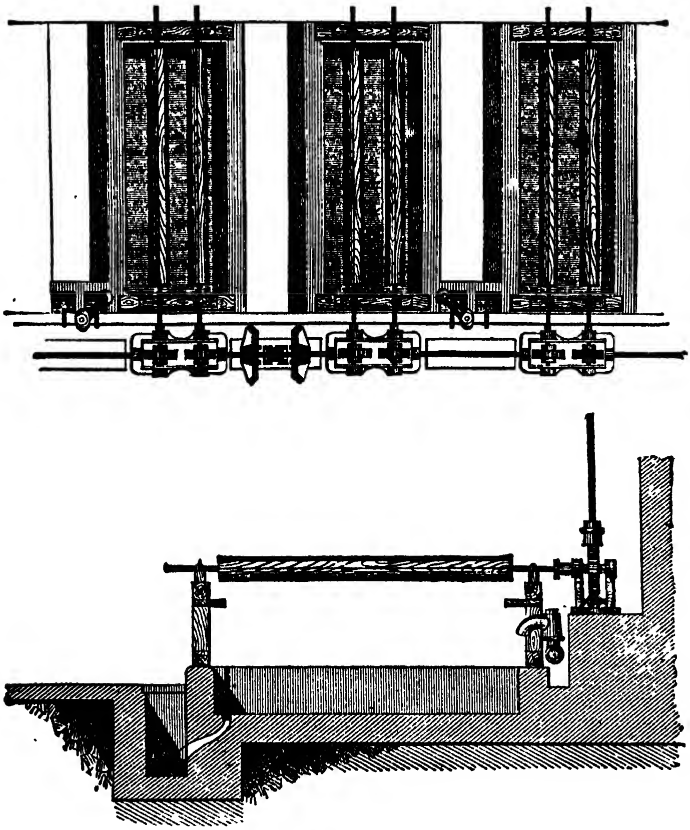
3 *Sour* with sulphuric acid 1° Tw. Wash well.

4. *Scald* (*i.e.*, boil in kier) for three to four hours with 2 to 3 per cent. soda ash.

5. *Reel* in bleaching powder $\frac{1}{2}$° Tw.

6. *Sour* in sulphuric acid $\frac{3}{4}$° Tw.

7. *Scald* for three to four hours with $1\frac{1}{2}$ to 2 per cent. soda ash.



Figs. 37 and 38.—Haubold's reeling machine for linen yarn.

8. *Dip*—*i.e.*, steep two hours—in bleaching powder $\frac{1}{6}$° Tw.

9. *Sour* in sulphuric acid $\frac{3}{4}$° Tw.

10. *Scald* for three to four hours with 1 to $1\frac{1}{2}$ per cent. soda ash.

11. *Dip* in bleaching powder $\frac{1}{10}$° Tw.

12. *Sour* in sulphuric acid $\frac{3}{4}$° Tw. Wash well and blue with smalt.

For a full white the yarn is given one or two more turns, according to the colour desired, using gradually weaker strengths.

13. *Scald* in 1 per cent. soda ash.

14. *Dip* in bleaching powder $\frac{1}{10}$° Tw. down to $\frac{1}{20}$° Tw.

After the lye-boils the yarn is usually well washed, first in the kier, and then once in hank-washing machines, which are also used after reeling. After souring and dipping, the washing is generally done by "swerking"—*i.e.*, filling up the vat with fresh water, and running off repeatedly until the yarn is clean. After the final wash, the yarn is squeezed through a squeezing mangle, and blued in a small machine similar to a hank-washing machine.

In boiling, the lye is first made up in the kier, and the hanks loosened and thrown in, care being taken to pack evenly, in order to prevent spots being formed.

Frequently the yarn is boiled only before weaving—*e.g.*, in 15 to 20 per cent. by weight of soda ash—and, if a greater reduction in weight is required, it is again boiled with 10 per cent. soda ash.

The loss in weight which flax yarn suffers in bleaching is recognised by the conditioning establishments to be 15 per cent. for a half-bleach, 18 per cent. for a three-quarters bleach, and 20 per cent. for a full bleach.

LINEN PIECES.

As is the case in the bleaching of cotton pieces, the methods in general use, although based upon the same principles, may vary considerably with regard to detail.

Broadly speaking, the following is the method at present generally followed in the North of Ireland:—

The pieces are first thread-marked with Turkey-red thread, sewn together end to end, run through lime water so as to take up 5 to 12 per cent. CaO, and are then boiled for eight to twelve hours in low pressure kiers holding 25 to 30 cwts. each. After liming they are washed in a rope-washing machine. At this stage the pieces are separated and made up into bundles (except in the case of very light linens, which are bleached throughout in the rope-form like cotton), and remain so through all the subsequent processes. The goods are next washed in wash mills, similar in construction to the wash stocks used for cotton yarn (*q.v.*), allowed to drain, and soured in hydrochloric acid at $1\frac{1}{2}°$ to 2° Tw. overnight, after which they are taken out, allowed to drain, and again mill-washed. Next follow the lye-boils, which are also effected in low-pressure kiers; according to the quality of the cloth, two to six boils are given for six to ten hours each, using a mixture of 1 part caustic soda and 3 parts soda ash at strengths varying from 6° to 4° Tw. In winter the lyes are taken slightly stronger than in summer. At certain stages between the boils the goods are "grassed" for two days, and in some cases "rubbed."

With very closely woven cloth they are frequently soured in sulphuric acid before the last boil. As a general rule light goods require two to three boils, medium goods three boils, and heavier and closely woven goods four to six boils, according to the time of the year.

After the lye-boils the goods are alternately treated with hypochlorite of soda and weak soda boils for three to five times, until sufficiently light in colour. Each of these series constitutes a "turn" or "round."

During these later stages the cloth also undergoes the process of "grassing" between each "turn," and in some cases rubbing before the last soda boil.

. The cloth is then steeped in large vats or "kieves" (dipping or chemicking) in very weak hypochlorite of soda, varying from $\frac{1}{10}$ per cent. chlorine for first dip to $\frac{1}{50}$ per cent. chlorine for last dip. After each dip the goods are soured in sulphuric acid varying from 2° to 1° Tw., and they are ultimately drawn by hand, allowed to drain, and mill-washed.

The lye-boils after the first dip are technically known as "scalds," and are carried out in the same kiers as the lye-boils, but only for three to four hours,

the strength of the lye being progressively weaker (from 3° to 1½° Tw. for last scald). From time to time the goods are "turn-hanked"—*i.e.*, each piece is re-hanked into a fresh bundle—so as to ensure every part of the web being treated equally.

The object of "rubbing" is to remove, by mechanical means, small black specks ("sprits") or streaks which appear in the goods. This is effected in a machine like that shown in Fig. 39. It consists of a framework on which are mounted three pairs of notched rubbing boards, B, underneath which there is a wooden vessel, V, in which the pieces are steeped in a strong soap solution. Of each pair of rubbing boards, the lower one is rigid, while the upper one receives, by means of a crank action not shown in the figure, a to-and-fro motion. The pieces are drawn through the rubbing boards by means of a

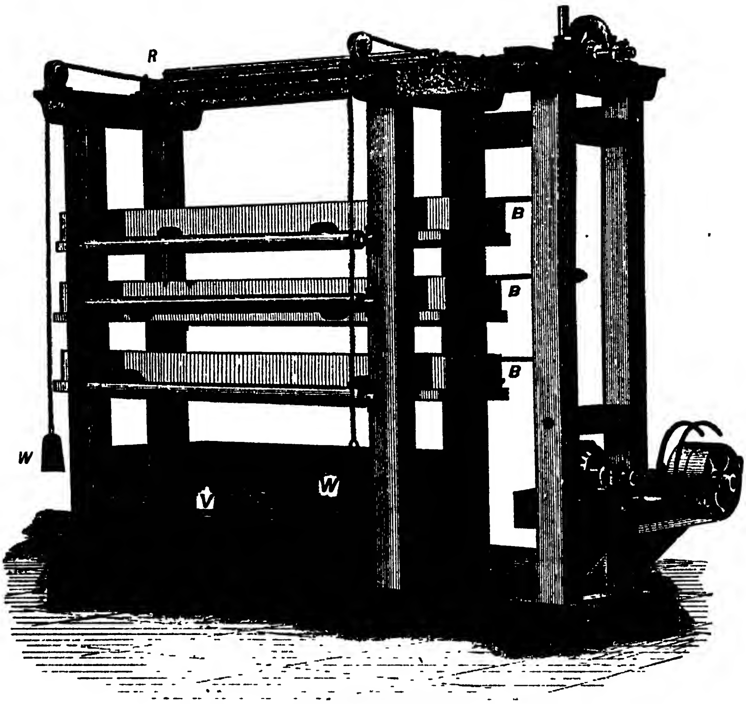


Fig. 39.—Rubbing boards for linen pieces.

pair of fluted rollers, R, at the top of the machine, the pressure of the rollers against each other being regulated by weights, W. The rubbing is continued until the black or yellow stripes are removed.

The term "mill-washing" is applied to an operation similar to washing in stocks in cotton yarn bleaching (*q.v.*).

The ordinary process of bleaching linen pieces occupies from three to six weeks. For densely woven material it is sometimes found advantageous to partially bleach the yarn before weaving.

In consequence of the enormous amount of time and labour involved in linen bleaching, the cost of production of white linen goods is materially increased, and any signal improvement which might be made in the way of cheapening the process would considerably benefit the linen trade. The

slow progress is not due to the want of initiative on the part of those interested, but chiefly to the risks which are run in experimenting with goods of so valuable a character. During the course of the past few years the Mather, Thies-Herzig, and other kiers of modern construction have been to some extent adopted, and caustic soda has here and there taken the place of lime, but the great bulk of the linen which comes into the market is still bleached by the old-fashioned process, which, though long and expensive, is known to give reliable results.

Cross and Parkes' Process.*—In ordinary boiling in vomiting kiers the proportion of liquor to goods is 7-10 to 1, while in kiers with forced circulation it has been possible to reduce this to about one-half this proportion. In the improved method the proportion is so far reduced that the process becomes one of steaming, in contact with the active solution, rather than boiling, and the circulation of the solution is consequently dispensed with.

The pieces are run at full width through a mixture heated to 30° or 40° C. of 1·75 lbs. soap (potash, fish oil, or soft soap), 14 lbs. silicate of soda (with a silicate ratio $Na_2O \cdot 3SiO_2$, and containing 30 per cent. SiO_2), 1·5 lbs. caustic soda, 1·75 lbs. oil (generally mineral oil of high boiling point, but in some cases a fatty oil or a mixture of a fatty and mineral oil), and 10 gallons water. They are then run into a chamber containing steam at atmospheric pressure, and are there wound into a roll. The goods are now steamed with dry steam at a pressure not exceeding 4 lbs. for one to four hours, and are then boiled (while still in the chamber) with soda or silicate of soda under pressure. After the boiling the goods are well washed. By this treatment linen goods are brought at once to the condition suitable for the dipping and first course of bleaching operations.

In the process of **de Keukelaere**,† the material to be bleached is first scalded for about half an hour in a lye containing 5 to 15 per cent. sodium sulphide, and is then rinsed in water containing ½ per cent. sulphuric acid on the weight of the linen. The operation of scalding is repeated twice or three times, and the bleaching is then proceeded with. It is claimed that by this process the organic matter and other substances which retard the bleaching are removed.

Bleaching by Ozone.—The necessity of "grassing" linen pieces in order to obtain a good bleach is associated with various drawbacks. It means that suitable fields should be available for the purpose in the vicinity of the works, and besides, that the weather and climate should be suitable for the purpose; furthermore, it entails a good deal of hand labour. With the object of replacing the grassing by a process which can be carried out in the works, and which is independent of weather and climate, an extensive series of experiments were carried out on a large scale by Messrs. Siemens & Halske at the Greiffenberg bleaching and finishing works in Silesia, in which ozonised air served as the bleaching agent.‡ Instead of being grassed the goods are run through hydrochloric acid, and exposed in the moist state in chambers to the action of ozonised air for about seven hours. Only one such treatment is necessary for a three-quarter bleach, while for a full bleach from two to three treatments are required, which alternate with the operations in the ordinary bleaching process as used for piece goods. Sunlight cannot, however, be dispensed with, and must be admitted to the chamber in which the goods are exposed to the ozonised air. In place of sunlight the electric arc light may be used. One day's exposure in the chamber is said to equal in effect three days' grassing. Bleaching by ozone is said to be no cheaper than grassing, but more convenient.

* *Journ. Soc. Dyers and Col.*, 1901, p. 38.
† *Ibid.*, 1905, p. 275.
‡ See also Andreoli, *Journ. Soc. Chem. Ind.*, 1897, pp. 92 and 93.

Although it would appear that good results may be obtained by the use of ozone in linen bleaching, its use for the purpose is at the present time very limited.

The use of **nitric acid** for the purpose of obviating the necessity for grassing has been patented in this country by Jardin.* To this end the goods are steeped for about five hours in a solution of 5 litres commercial nitric acid in 1,000 of water in place of the first grassing. No further indication is given in the specification regarding the composition of the bath in the subsequent treatment. The treatment with nitric acid is each time preferably preceded by an alkaline treatment. In his claim Jardin also includes the use of one or more oxygen compounds of nitrogen.

Hydrogen peroxide and **permanganate of potash** are also capable of giving good results as bleaching agents for linen, and are used to some extent for the purpose.

Brown Holland.—The colour of brown holland is not usually produced by dyeing, but by running the unbleached linen pieces through a warm solution of stannous chloride acidulated with sulphuric acid. An acidulated solution of titanous chloride may also serve for the purpose.

BLEACHING OF HEMP.

A full bleach on hemp is seldom desired, although this can be effected by processes similar to those adopted for linen. At the Paris Exhibition of 1889 there were several exhibits of beautiful white hempen fabrics, which strongly resembled linen in appearance.

For string and light ropes a rough bleach is sometimes employed. For this purpose the goods are first boiled for half an hour in a solution of 10 kilos. silicate of soda at 70° Tw. in 500 litres water. They are then boiled in water alone, after which they are rinsed and steeped for 24 hours in a solution of 10 kilos. bleaching-powder in 1,500 litres water. After being allowed to drain they are hydro-extracted and soured in hydrochloric acid (1 litre commercial hydrochloric acid in 1,000 litres water). They are then well washed in water, and dried. A better white is obtained by repeating these processes.

BLEACHING OF JUTE.

Although the modes of manufacture and commercial applications of jute have advanced with such rapid strides since it was first introduced in Europe as a textile material, yet, as regards its bleaching, the success does not appear to have been so marked; for there is little doubt that, to a large extent, the same processes are still carried out as were in operation when first it became of commercial importance. Probably this may be accounted for by the fact, that it is not necessary for the bleached fibre to have such a degree of purity as is required, for example, in the case of flax or cotton, for whereas with the latter it is essential for the production of delicate shades of colour, with jute, sufficient delicacy can be obtained from either the cream or light straw-coloured material.

After bleaching it is divided, broadly speaking, into two classes according to the final shade required on the yarn, one being known as the "Half Bleach," and the other as the "Full Bleach." The former is a straw, and the

* *Journ. Soc. Dyers and Col.*, 1904, p. 105.

latter a light cream colour, this difference being utilised principally in the subsequent dyeing operations, as, for all purposes where dark shades are required, either the raw or "Half Bleach" is invariably used, whereas for light shades the "Full Bleach" quality is necessary.

Bleaching of Jute Yarn.—The following is an outline of the general method of bleaching jute yarn at present carried out in the Dundee district.

First Method.—The hanks are sorted into bundles of from 6 to 8 cwts. each, according to the size of the vessel, then suspended on smooth wooden rods, and immersed in a rectangular tank filled with water containing the necessary amount of bleaching-powder solution. Each separate rodful of yarn is taken, swayed once or twice to and fro, and then carefully lifted, so that the exposed portion of the yarn may easily be placed in the liquid. This lifting is performed either by the workmen, or preferably by an arrangement of levers, whereby the whole of the yarn is immersed in the bath and easily moved therein without any portion becoming exposed to the air. After remaining in this bath for one hour, at a temperature of 80° to 100° F., the liquid is run off and the hanks allowed to drain. They are then washed and placed in a similar tank containing dilute sulphuric acid, from which, after remaining a quarter to half an hour, they are withdrawn, and again well washed in successive quantities of water.

Quantities of Materials, &c.—Yarns, 6 cwts.; bleaching-powder solution, 8° Tw., 120 gallons; temperature, 100° F.; sulphuric acid, 144° Tw., use 1 gallon for souring.

These proportions are used in order to obtain the ordinary "Half Bleach," but, if a lighter colour should be required, the operations are repeated, using 80 gallons of the bleaching-powder solution without previous souring.

Second Method.—In this method the bundles of yarn, weighing about 10 cwts., are treated in a series of tanks containing solutions of bleaching-powder of different strengths. Usually there are three tanks, the first containing 15 to 20 per cent. bleaching-powder (calculated on the weight of material), the second 10 to 15 per cent, and the third 5 to 10 per cent.; the yarn is allowed to remain in each tank for from half to three-quarters of an hour at a temperature of 120° F. (48° to 49° C.). It is then washed and passed into the acid bath containing sulphuric acid at 1° Tw., where it remains half an hour; finally it is well washed and dried.

One great advantage obtained by this method is, that the yarn, which appears very uneven after treatment in the first tank, need not remain so long in the strong solution of bleaching-powder as is necessarily the case with the first method, because the reaction is started in this solution and finished in the weaker ones. It is also interesting to note that, whenever tendering of the yarn does take place, it always occurs in the first tank, so that the time of treatment is regulated by the quality of the yarn, which also regulates the use of calcium hypochlorite or sodium hypochlorite; for with certain yarns better results are obtained with the calcium salt than with the sodium salt and *vice versâ.* The treatment of the yarn during spinning has also some slight effect upon the bleaching operations, as it is necessary, whenever mineral oils have been used, to steep the yarn in hot water, and, in some rare cases, in a weak alkaline bath, previous to immersion in the bleaching-powder; but, with certain other oils, as, for instance, whale oil, this is not necessary. The most striking difference between the bleaching of jute and cotton is, that the jute is rarely, if ever, treated with alkali, the principal reason being that this occupies too much time, and is, therefore, too expensive; besides, the yarn loses too much in weight, while the final results are little better than that produced when the alkaline treatment is neglected. The total loss in weight which the yarn undergoes in bleaching varies from 6 to 8 per cent.

For Jute Pieces, Cross & Bevan recommend the following process:—

1. The pieces are first treated with a solution of silicate of soda (4·8 kilos. silicate to 1,000 litres of water) at 70° C.

2. They are then passed through chloride of soda (sodium hypochlorite) prepared from chloride of lime and sodium carbonate, and made of such a strength as to contain about 0·7 per cent., but not more than 1 per cent., available chlorine. The presence of soda completely prevents the formation of chlorinated products.

3. After being well rinsed, the pieces are passed through dilute hydrochloric acid (½° Tw.) to which a small amount of sulphurous acid has been added. The object of this treatment is to remove basic compounds which might subsequently, by the action of oxidising agents, bring about a discolouration of the fibre, and at the same time to dissolve away salts of iron. Wash and dry. The goods exhibit at this stage a light cream colour, possess a soft handle and a good lustre, and are ready to be dyed. But if intended for printing they must undergo the following process:—

4. Pass through a bath of bisulphite of soda containing from 1 to 2 per cent. of sulphurous acid, squeeze out the excess of liquid, allow to lie for two or three hours and dry on steam cylinders. By the drying, the sulphurous acid is driven off and the pieces leave the drying cylinders evenly impregnated with neutral sulphite of soda, which protects the fibre from the oxidising influences to which it is exposed in steaming, but does not prevent the development of the printed colours.

Properties of Bleached Jute.—Although it is generally supposed that during bleaching, the jute fibre suffers from the action of chlorine, this solely depends upon the quality of the yarn; for, with the better qualities, and by careful treatment, it is difficult to detect any deterioration whatever.

Chlorine does not act upon dry jute, even when the temperature is raised to 100° C., but in the presence of water, combines rapidly and with the evolution of heat. This chlorinated derivative is of a yellow colour and is soluble in alcohol, from which solution water precipitates a compound having the formula $C_{19}H_{18}Cl_4O_9$, as a yellow flocculent mass, which gives, when freshly precipitated, the characteristic magenta colouration with sodium sulphite.*

One remarkable feature of bleached jute is the change which it undergoes when left exposed to the air; for, not only does it turn brown and darker in colour, but the fibre itself also seems to suffer, as it is slightly tendered, and becomes harsher and more brittle. This change is brought about more by temperature than by the presence of air.

WASHING AND BLEACHING OF WOOL.

LOOSE WOOL.

As wool comes into the market, it usually represents a very impure article, containing from 30 to 80 per cent. of foreign substances. The impurities with which it is contaminated may be roughly classed under three headings, viz.:—

1. Fatty or wax-like bodies soluble in such solvents as bisulphide of carbon, benzene, or petroleum ether. This portion is generally known as the *yolk* or *wool-grease.*

2. Bodies soluble in water, consisting chiefly of the potassium salts of a number of organic acids. This portion is known as the *suint.*

3. Mechanically adhering impurities (earth, &c.) which adhere to, or are enveloped by, the suint and yolk.

* *Journ. Chem. Soc. Trans.*, 1882, p. 98.

Yolk or *wool-grease* consists principally of the higher solid alcohols, cholesterin and isocholesterin, in the free state and in combination with oleïc and fatty acids, principally stearic and palmitic. These bodies, though difficult to saponify under ordinary circumstances, form emulsions with soap solutions, and can, therefore, be removed by soaping or by treatment with one of the solvents above named. To what extent exactly the wool-grease is removed by soaping or by treatment with solvents has not yet been definitely ascertained, but their effect appears to be restricted to the removal of those impurities only which envelop the fibre, and not of the grease contained in the interior of the fibre.*

The *suint* consists principally of the potassium salts of oleïc, stearic, acetic, valeric, hyaenic, and other organic acids.† It contains besides, nitrogenous substances, and small quantities of phosphates, chlorides, and sulphates.

The mechanically adhering impurities, lastly, consist chiefly of earthy matter (the composition of which varies with the nature of the soil on which the animals have been bred) and *burrs*. The latter are especially prevalent in Botany wool, and as it is impossible to completely remove them by mechanical means, they are destroyed before spinning or after weaving by *carbonising* (*q.v.*).

The fleece is frequently washed on the sheep's back,‡ before shearing, with cold water, but only a portion of the impurities are removed by this treatment. The bulk of the wool which comes into the market is "in the grease."

A thorough cleansing of the wool previous to its further mechanical or chemical treatment is of fundamental importance in the production of worsteds or woollens of good quality, any negligence in this respect being difficult to rectify after spinning, weaving, dyeing, or carbonising. This is due to the fact that yarn and fabrics are not so easily cleansed as loose wool, while any suint remaining in the latter is driven into the fibre by the various operations of dyeing, carbonising, or steaming (crabbing, decatising), so that it cannot be removed by scouring as readily as from loose wool. Wool, from which the fatty impurities are not completely removed, is liable to resist the action of mordants and dyestuffs, with the result that in dyeing the colours come out uneven or cloudy, or that they "rub."

Wool Sorting.—In one and the same fleece the quality of the wool varies considerably, that from the shoulders being the finest, that from the back and lower parts of the sides being usually of somewhat inferior quality, while that from the legs, belly, and other parts is the least valuable. Previous to wool washing or scouring, it is usual to sort out by hand the various qualities ("matchings" or "sortings"), and to treat them in the subsequent operations of washing, preparing, combing, spinning, &c., separately. The men engaged in this particular operation were formerly often the victims of a dangerous malady known as "wool sorter's disease," or anthrax, which was found to occur more frequently among those dealing with certain classes of wool (especially mohair) than among others. The operation of sorting is now conducted on tables covered with wire netting, through which a powerful down draught is maintained, thus preventing the inhalation by the operator of the dust which falls from the fleece. By this simple contrivance the occurrence of the disease has been, to a large extent, prevented.

Preliminary Washing in Water.—As mentioned above, it is sometimes customary to wash the fleece on the sheep's back before clipping. In many works this process is carried out with the raw wool as it comes into the hands

* See *Journ. Soc. Dyers and Col.*, 1890, p 18.

† *Journ. Soc. Dyers and Col.*, 1886, p. 133

‡ Colonial wools are sometimes washed in this way in order to lessen the cost of carriage.

of the manufacturer, but in such cases the extraction is conducted systematically with warm water on the counter-current principle.

A scheme for carrying out the washing of raw wool on this principle is illustrated in Fig. 40. The system consists of three (or more) vats, A, B, and C, which are so arranged that the wash-water will fall by gravitation from A to B and B to C. The wool to be extracted is loosely packed in crates, *a*, *b*, *c*, which can be removed from one vat to the next by means of any suitable device. When the scheme is in work all three crates are filled with wool, which is allowed to steep in the warm water (or liquor) for some 10 to 20 minutes. The crate *a* is then removed, the liquor being run out of vat C, which is filled with the liquor from vat B, while the liquor from vat A is run into vat B. Crate *b* is then transferred to vat A, crate *c* to vat B, while a crate with untreated wool is let into vat C, and vat A is filled with clean

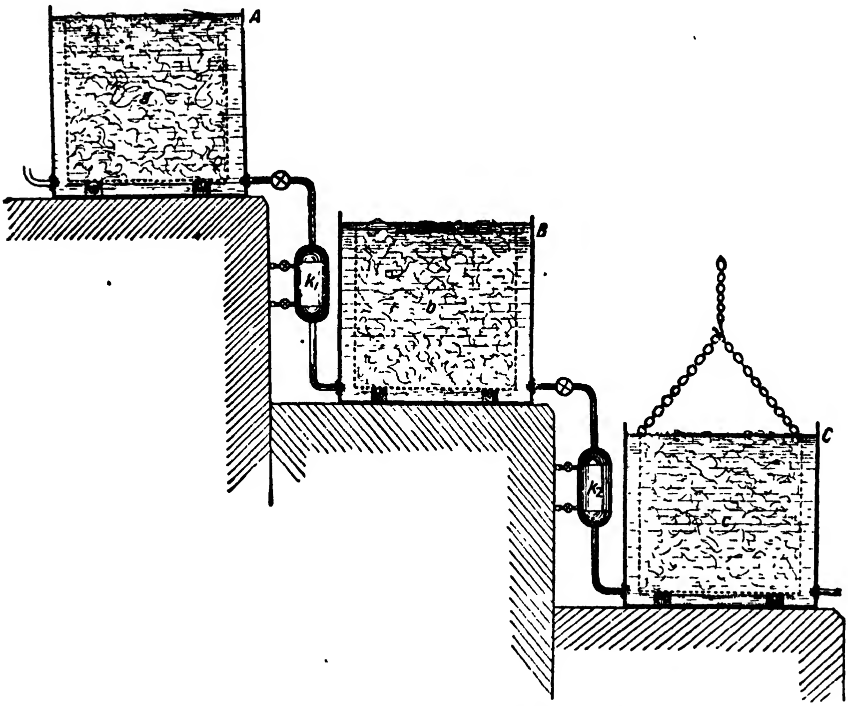


Fig. 40.—Scheme for extracting wool with water.

water. In this manner the wool which has already been twice washed in vats C and B comes into contact in vat A with clean water, which takes out the remaining soluble impurities. At the same time no unnecessary dilution has taken place, and the concentration of the liquor in vat C is practically three times as great as if the extraction had been effected in the ordinary way. The temperature of the water is maintained at about 45° C., and this may be conveniently effected by means of steam kettles, k_1 and k_2.

A more rational method of extracting can be effected by extracting the wool in vertical cylinders, using the same principle of counter-current, and not transferring the material from one vessel to another, but treating it *in situ*, the circulation (and simultaneous heating) of the liquors being effected by means of steam injectors, and the distribution by a system of pipes.

In either case the muddy brown-coloured liquors, which contain the greater part of the *suint*, are evaporated to dryness (preferably in multiple-effect evaporators), and the residue is calcined in a reverberatory furnace. The ash thus obtained consists chiefly of potassium carbonate, which can be extracted from it by water. This solution, evaporated to dryness and calcined, yields a very good quality of potash.

This process of extraction would, no doubt, be more universally adopted were it not for the fact that it entails a considerable diminution in the yield of wool-grease obtained in "cracking" the wash-waters from the washing proper. The loss in grease is partly due to the direct solubility of some of the potash salts of the higher fatty acids, but more so to the emulsifying of a portion of the wool fat in the solution of the suint, which acts like a soap.

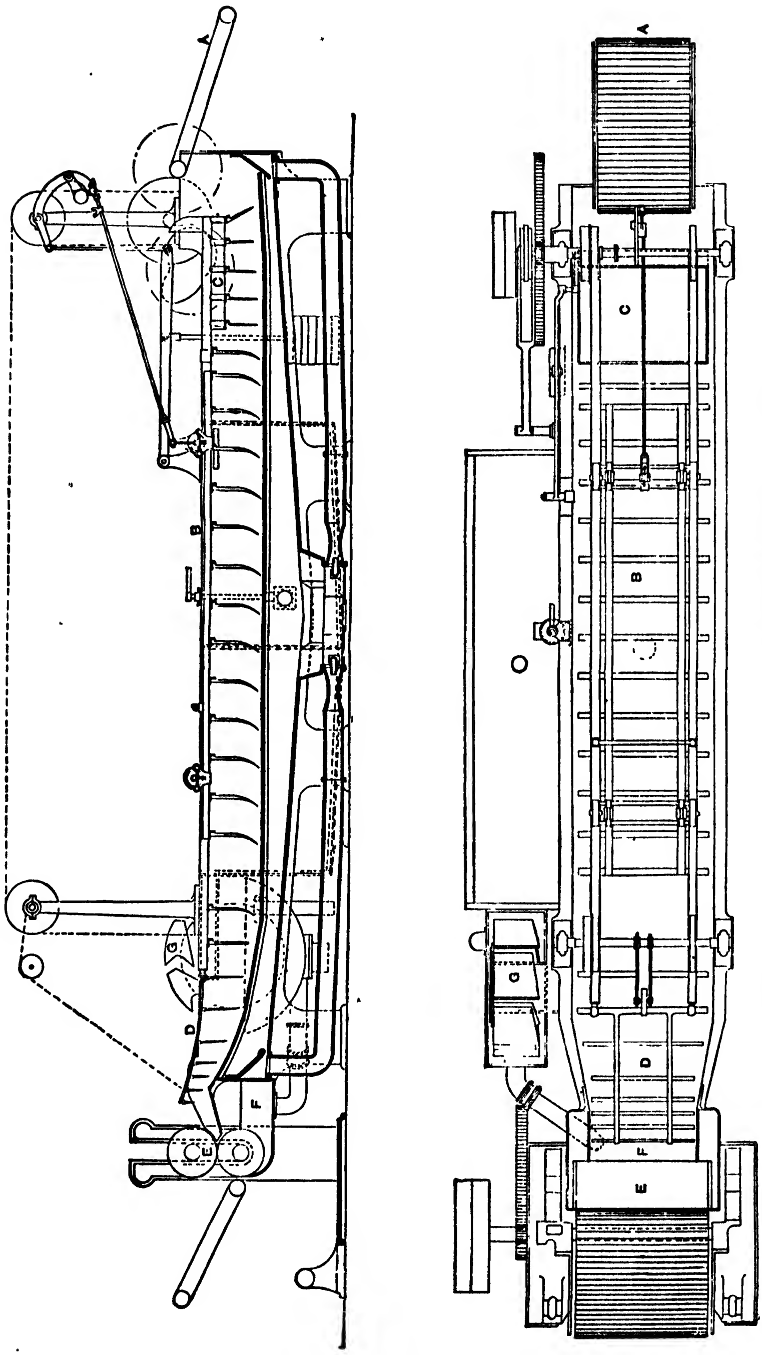
Washing or Scouring.—This operation, which follows the sorting and lixiviation with warm water (where such has been used), is generally carried out by the manufacturer, or, when the wool is to be dyed in the loose state, by the dyer.

Formerly, wool was washed with stale urine (the active constituent of which is supposed to be ammonium carbonate), but this means, although still used in a few isolated cases on the Continent, may be said to have been almost entirely superseded in England by washing with soap and alkali. For use, the stale urine is mixed with about five times its volume of water, and the liquor is heated to 40° to 50°. In Yorkshire, the largest centre of the woollen and worsted industries, the following simple process is almost invariably adopted. The wool is washed in three successive soap-baths, after which it is squeezed and dried in a current of air. The operations are seldom carried out by hand, but generally in specially constructed machines, described below.

For the finest qualities of wool, a soft soap prepared from Gallipoli oil is used. For the less fine qualities the soap is assisted in its action for cheapness' sake by additions of potassium carbonate, sodium carbonate, or silicate. The addition of sodium salts to a potash soap is, however, irrational, since a soda soap is thereby formed by double decomposition, and the advantages which it is intended to gain by the use of the more expensive potash soap are thus to a large extent nullified. Cheaper qualities of soap are also frequently employed. The amounts of soap, or of soap and soda, necessary for washing vary considerably for the various qualities of wool, and are determined by practical experience. So-called pitchy wools, which contain a large amount of wool-grease, require most.

The temperature of the soap-baths used in washing wool should, according to F. H. Bowman, not exceed 35° C., if all the valuable properties of the fibre, more especially the lustre, are to be preserved. In working on the large scale this rule is, however, not often observed, considerably higher temperatures being employed.

Figs. 41 and 42 show in section and plan the construction of a wool-washing machine made by Messrs. T. & W. M'Naught, of Rochdale. It consists in the main of an iron tank (20 to 30 feet in length and about 3 feet broad, with a capacity of 650 to 1,300 gallons) provided with an automatic arrangement of forks or prongs, by which the wool is made to pass slowly through from the entrance to the delivery end. The raw wool is fed evenly on to the travelling apron, A, and is at once pressed, on entering the machine, beneath the surface of the suds by means of a perforated tray, C, called the immerser. Here it is seized by the prongs of the iron frame, B. The action of this frame is as follows:—It is lowered until the prongs are immersed in the suds, and whilst they are so immersed the frame makes a stroke forward. At the end of this the frame is lifted up until the prongs are clear of the suds, when a backward stroke is made, and the prongs are again immersed and moved



Figs. 41 and 42.—Section and plan of M'Naught's wool-washing machine.

forward, and so on repeatedly. After a few strokes, a constant circulation towards the squeezing rollers is set up in the suds, the effect of which is to float the wool forward, almost without the assistance of the prongs, the point claimed being that it is scarcely touched in its passage through the tank save by the liquor. The delivering or lifting motion, D, consists of a light frame with prongs hinged to the main frame, which is kept suspended by a chain. The points of the prongs follow the curved incline of the false bottom. The level of the suds is at the top of this incline, and the wool is partly floated and partly pushed over, after which it slips down fully charged with suds to the squeezing rollers, E. The liquor expelled here is caught by a small receptacle, F, below, and is lifted back into the tank again by a bucket wheel, G. The squeezing rollers are weighted, the pressure being given by a dead weight, which is conveyed through a spiral spring on the top levers.

Self-acting arrangements are provided for cleaning or flushing out the tank without removing the false bottom plates. By means of ejectors placed underneath the middle of the machine, a rapid circulation is given to the dirty water under the false bottom, when the tank has nearly run out, and thus the mud and dirt are carried off with the last portions of the water. If necessary, the bottom may then, in the same way, be washed over again with a little clean water.

A complete installation for wool washing consists of three machines.* The makers recommend for the first machine a capacity of 1,300 gallons; for the second and third, however, a capacity of only 650 gallons each. By adopting these dimensions the tank of the first machine is capable of holding double the quantity of impurities in the space beneath the false bottom before a change of water is necessary, whilst the washing power is increased twofold where it is most required. As the soap solution is discharged from the wool by the squeezing rollers at the end of the last machine, it is collected in a small receptacle, whence it overflows and passes through pipes to the side of the machine; the cleanest part of it is there lifted by revolving buckets into the tank, and the remainder run on to the second machine, precisely the same action taking place between the second and first machines. But the discharge water from the squeezing rollers of the first machine is allowed to run away to the main drain, or to be collected so as to extract the grease from it, which is usually done by large firms. The dirty water which eventually passes away from the machines in the manner described is replaced from an auxiliary tank, containing a quantity of clean water already charged with the necessary amount of soap, and heated to the proper temperature ready for use.

The drying of loose wool after washing may be done in the open air, but this process is seldom resorted to in England owing to the space required and the uncertainty of the weather. A simple contrivance largely adopted by wool washers consists of a flat table covered with galvanized wire netting, through which a current of heated air is sent from below by means of fans. The wool is spread evenly on the netting, and is thus dried in a short time.

Machines are also constructed by various makers, in which the drying is effected continuously, the wool being passed along aprons or endless bands through a chamber in which it meets a current of hot air.

BYE-PRODUCTS OBTAINED IN WOOL WASHING.

Wool-grease.—In most small works the waste water obtained from wool washing is allowed to run away, but in the better regulated and large establish-

* The third or last tank contains a weak solution of pure soap only. To the solution in the first machine a further addition of soap and usually sodium or potassium carbonate is made. It has been recommended to use water only in the last machine, but in practice this has not been found to give satisfactory results.

ments this waste water is specially treated for the purpose, not only of getting from it the fat contained in the wool, but also of regenerating the fatty matters from the soap used in washing.

For this purpose the waste water, which consists essentially of an emulsion of the wool-grease in soap solution, is first allowed to settle in large tanks, in order that the coarser solid impurities may sink to the bottom. An excess of crude sulphuric acid is then added, which decomposes or "breaks," the soap and the fatty acids rise to the surface, bringing with them the whole of the wool-grease in the form of a dirty-looking magma. After the greater part of the water has been got rid of by allowing the magma to drain on canvas filters, it is packed in sheets of canvas and hot-pressed. The liquefied wool-grease thus obtained is then heated in metal vessels until the greater part of the solid impurities has settled, when it is run into casks where it solidifies. In some works the cake from the process is extracted with bisulphide of carbon, in order to obtain the last portions of the wool-grease which mechanically adhere to it. Wool-grease or "Yorkshire grease" is used as a lubricant, and for smearing sheep in winter in cold climates, while a large proportion of what is produced is distilled for the manufacture of stearin and oleïn. Many attempts have been made to utilise it for the manufacture of soap, but although this is not impossible, the expense is prohibitive.

Another method* of regenerating the wool-grease is to precipitate with calcium chloride, which throws down the soap as an insoluble lime-soap, and along with it the wool-grease. The magma is then treated with hydrochloric acid for the purpose of decomposing the lime-soap and removing the lime. The further treatment is the same as in the first method.

In some works a pure form of wool-grease is obtained from the waste wash-water by passing the clarified (and preferably concentrated) liquor through centrifugal machines running at a very high speed, such as are used in creaming milk. By again emulsifying the grease thus obtained, and passing it for a second time through the centrifugal machine, a creamy white substance is obtained, to which the name of *Lanolin* has been given, and which finds extensive application in pharmacy for making up salves, &c.

Wool Washing with Volatile Liquids.—Numerous endeavours have been made from time to time to dispense altogether with the use of soap in the washing of wool, the objects being to cheapen the operation and to obviate the injurious effects of the hot or warm soap solution, which causes to a certain extent a felting and diminution in the lustre of the fibre.

The principle proposed by Singer & Judell is to pass the wool, which is carried between two endless bands of brass wire netting, first through a series of vats containing bisulphide of carbon. The excess of liquid is squeezed out of the wool as it leaves each vat by means of a pair of rollers. The endless band containing the wool then passes in a similar manner through a series of water tanks, in which the suint and the mechanically adhering bisulphide of carbon are removed. The whole machine is covered by a hood, which is hermetically sealed by water seals at all points except where the endless band enters and passes out again, and a small opening at the top by means of which a gentle current of air is maintained through the apparatus.

Both in the bisulphide and in the water tanks the counter-current system is adopted, so that the regeneration of the pure wool-grease and of the potash are mere matters of detail. The saturated bisulphide flows from the last tank into a specially constructed retort, from which the molten wool-grease is obtained in a continuous stream, while the fresh distilled bisulphide is passed again into the machine.†

* See *Journ. Soc. Dyers and Col.*, 1888, p. 197.
† *Journ. Soc. Dyers and Col.*, 1889, p. 19.

Burnell's machine consists of two wrought-iron vessels, in the first and larger of which the wool is caused to pass slowly through petroleum spirit, being pressed in its passage through the liquid by means of a series of about twenty rollers against a large central cast-iron bowl or drum. In the second vessel the wool is similarly treated in warm water. The counter-current system is also adopted in this machine, and the bye-products may be recovered as in the foregoing system.*

Neither of these processes appears to be in practical use at the present time.

According to another process, patented by Mertens,† the wool is extracted in a series of upright iron cylinders with petroleum spirit on the counter-current principle. After the wool has been extracted three (or four) times, it is dried *in situ* by means of a current of heated carbon dioxide. It is then extracted with water in order to remove the suint. The process is successfully carried out by the "Solvent belge" in Verviers and elsewhere.

Extraction by means of volatile solvents is the only rational means of cleansing those portions of the fleece contaminated with paint or tar which has been used by the farmer for the purpose of identifying the sheep.

WOOLLEN AND WORSTED YARN.

As they are delivered to the dyer, most woollen and worsted yarns contain oil which has been purposely added in order to facilitate the spinning. The oils used for the purpose are usually non-drying vegetable oils which readily emulsify with soap solutions, such as olive oil, cotton-seed oil, oleic acid (olein), and, latterly, ricinoleic acid,‡ while some spinners employ Turkey-red oil. The use of mineral oils for the purpose is to be strongly deprecated, since they are very difficult to remove by scouring. According to H. S. Smith,§ the use of oil of any kind has a deteriorating effect on the ultimate fabric as far as colour and finish are concerned. Worsted yarns contain, on an average, about 2 to 3 per cent. of olive oil, while the amount of oil put into shoddy yarn may in some cases exceed 15 per cent. of the weight of the material. Worsted yarns spun on the French system (mule-spun) contain no oil.

It is necessary to wash or "scour" the yarn for the purpose of removing the oil before it can be dyed or bleached. If this is omitted, the presence of the oil will cause the yarn to wet out badly and unevenly, and uneven dyeing may result. For cheap blacks the scouring is sometimes omitted.

Some yarns, especially those made from lustre wool, have the property of "curling" when brought in contact with water to such an extent that the whole hank might become entangled. In order to avoid this, such yarns are "stretched" before scouring. For this purpose the hanks are tightly stretched on a frame like that shown in Fig. 43, consisting of two double rows of spindles, C, mounted on two iron beams, A and B, of which A can be moved away from or towards B by means of set screws, D. When filled, the frame is immersed in boiling water for about half an hour, then taken out and allowed to cool. The position of the hanks on the spindles is then changed by turning them half round, and the frame is again immersed in the boiling water for some minutes. The yarn thus becomes evenly stretched, and is found to have completely lost its property of curling. By means of an improved arrangement, patented by Frusher, a second stretching is rendered unnecessary, the spindles or arms of the stretching frame being caused to revolve slowly.

* *Journ. Soc. Dyers and Col.*, 1900, p. 2.
† See also *Textile Colorist*, 1906, p 65.
‡ *Journ. Soc. Dyers and Col.*, 1905, p. 170.
§ *Ibid.*, 1904, p. 77.

In this process the wool fibres, rendered plastic by the action of the boiling water, are subjected to considerable tension which straightens them. On cooling under tension they retain the shape imparted to them by stretching at the boiling temperature. The same principle is adopted in the "curling" of worsted yarns used in the manufacture of imitation "astrachan" and other fabrics. To obtain this effect the yarn is twisted as tightly as possible, tied in this position, and boiled in water. On cooling and opening out, it is found to be curled.

The scouring is done with a solution of soap, or of soap and soda (4 per cent. soap and 3 per cent. soda are usually sufficient), at a temperature of 35° to 45° C. In some works the operation is conducted in rectangular

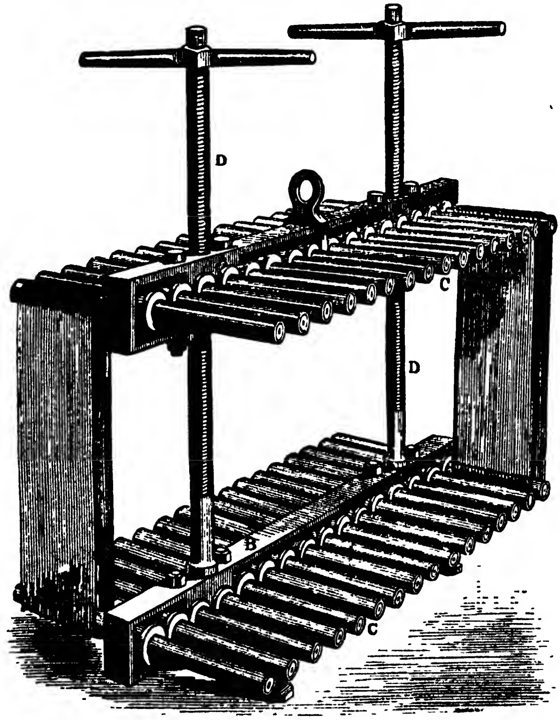


Fig. 43.—Stretching frame for worsted yarns.

wooden vessels, heated by steam, capable of holding on an average 100 lbs. of yarn. The hanks are suspended in the soap solution on sticks which lie across the vat, and are turned two or three times, after which they are taken out and washed in water to remove the surplus soap solution. They are then hydro-extracted, and are ready to be dyed.

A simpler and more rapid method consists in turning the hanks two or three times by hand in the soap solution which is contained in a square wooden vat, at the side of which there is a pair of squeezing rollers with a travelling apron leading up to them. The rollers may be constructed of cast iron, and covered with some soft protecting material (such as silk noils) to prevent the yarn being damaged. To prevent any damage to the yarn by too sharp a nip, springs are interposed between the screws regulating the pressure and the bearings of the top roller.

In working by this method, the operator always has two hanks in the liquid, one of which he turns while the other is allowed to soak. The one which he has turned two or three times he throws on to the travelling apron, by which it is carried to the squeezers. Before beginning to turn the second hank he puts a fresh one in to soak, and so on. After scouring, the hanks are washed and hydro-extracted.

Although several machines have been devised for washing woollen and worsted yarns, they have met with little favour among dyers. One arrangement of this kind consists of a rectangular wooden vat containing the soap solution. At one end there is a travelling apron and a pair of squeezing rollers, while over the vat are three bobbins which have an alternate backward and forward motion. The yarn is suspended on the bobbins, and the turning, otherwise done by hand, is done by the machine. There does not, however, appear to be any saving in labour since some one must be there to put on and take off the hanks from the bobbins. It is questionable whether such a machine offers any advantages over the method of washing by hand.

In dealing with large quantities, the hanks are sometimes tied loosely together, end to end, with string, and passed in rope-form two or three times up and down through the soap solution, and then through a pair of squeezing rollers covered with some soft material.

The *waste waters* from the washing of woollen and worsted yarns consist essentially of an emulsion of oil in soap, and should not be allowed to flow away, since the regeneration of the soap does not present any difficulties. It suffices to run the waste waters into tanks, add an excess of sulphuric acid, and collect, drain, and hot-press the resulting magma of fatty acids and oil. The resulting grease can easily be converted into soap by boiling with the necessary amount of caustic alkali or of a mixture of carbonate and caustic.

WOOLLEN AND WORSTED PIECES.

In the manufacture of plain goods it is not usual to scour the yarn before weaving; such pieces, therefore, contain all the oil which was originally contained in the warp and weft. For common blacks or heavy woollens, the oil is frequently left in, the pieces being mordanted and dyed without scouring previously. Low class worsted coatings are simply washed in soda and then steamed. But for better class blacks and for colours, all piece goods are first scoured in soap or in soap and soda.

Generally this is effected in a washing machine known as a "dolly" (see Fig. 44).

The machine consists essentially of a large wooden trough, V, seated on brickwork, and provided with a pair of squeezing rollers, A B, two guide rollers, C D, and a small trough, T. The pieces to be scoured are stitched together end to end (four to five or more), and run in the direction shown by the arrows from the warm soap liquor in V through guide pegs (not shown in figure) over roller, C, and thence between the pair of heavy wooden bowls, A B, of which A is direct driven, while B, which runs in slotted bearings, merely presses with its own weight against A. The dirty liquor which is thus expressed from the pieces falls into trough, T, and flows away. After passing through the squeezers, the pieces pass over the guide roller, D, back into the main trough, V, then again through the guide pegs and squeezing rollers, and ultimately pass out at the left-hand side of the machine. Fig. 45 shows a perspective view of a machine of this kind. In the improved machine of L. P. Hemmer, the squeezing bowls are ribbed or fluted, and this arrangement is said to offer considerable advantages over the plain bowls, inasmuch as the

action of the detergent is thereby amplified, while the pieces are not so liable to lap round fluted rollers as round smooth ones.

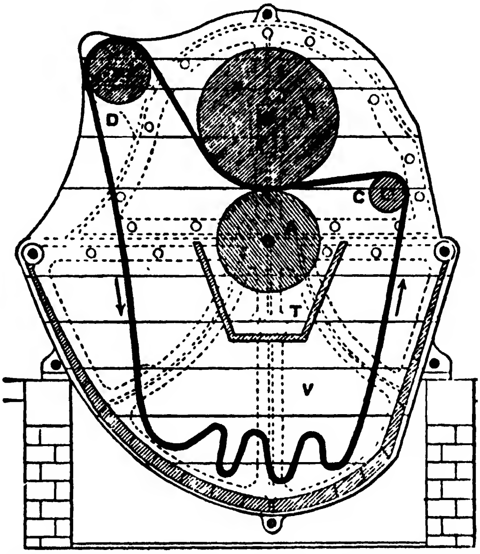


Fig. 44.—Washing machine (dolly) for woollen pieces.

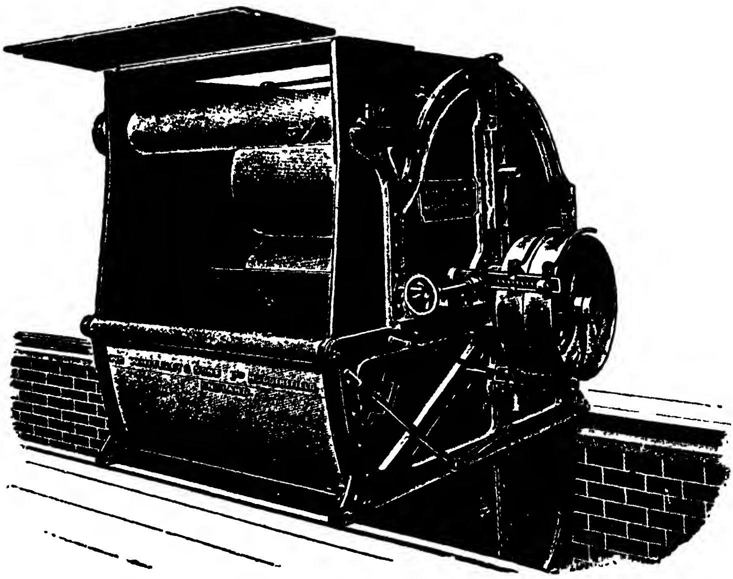


Fig. 45.—Washing machine (dolly) for woollen pieces.

For pieces which are liable to crimp or crease the dolly is not suitable. Such goods are washed in broad-washing machines, one of which is shown in

Fig. 46. In principle these machines are similar to the dolly, the only essential difference being that the pieces are made to pass through the rollers and the scouring liquid at full breadth instead of in rope-form.

After scouring, the goods are washed in water to remove the soap.

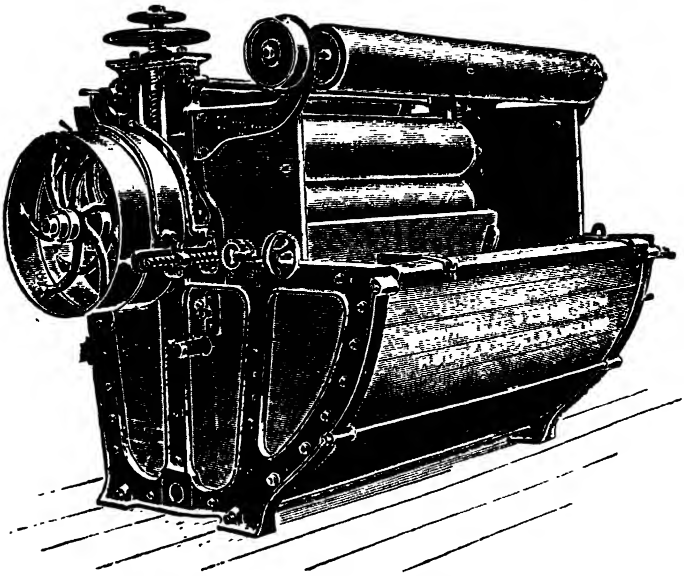


Fig. 46.—Open washer or broad-washing machine.

Broad-washing machines are also found especially useful in washing after milling, preparatory to dyeing, owing to the thorough manner in which they remove the impurities. In many works they have, to a large extent, taken the place of the dolly.

WORSTEDS AND UNIONS.

Pieces made with cotton warp and worsted weft "cockle" when put into water—*i.e.*, the surface of the piece becomes uneven owing to the different degree of contraction of the two fibres. By stretching, or drying in a stretched state, this unevenness can be overcome, but it will show itself again as soon as the material gets wet. The same defect shows itself, though in a more limited degree, in worsted fabrics in which the warp and weft are made of different classes of wool.

Crabbing.—Such goods are subjected before scouring and dyeing to an operation termed "crabbing," which is analogous to the stretching of worsted yarn, and which causes the setting of the piece in such a manner that it does not cockle when wetted. In crabbing, the pieces are drawn at full breadth and under considerable tension through boiling water, beamed and allowed to cool. They then retain the stretched position in which they were beamed, provided that they are not subsequently subjected to a higher temperature than that of the water through which they were drawn.

The principle of the crabbing machine is shown in Fig. 47. The goods wound tightly on the beam, A, are drawn under great tension (produced by means of a brake, *b*, on beam, R) through boiling water contained in the trough,

A, by the bowls, B and C, of which C is direct-driven, while B rests with its own weight on C and is carried in slotted bearings. The pieces are thus wound evenly and under considerable pressure and tension on to B.

Fig. 48 shows a crabbing machine with iron rollers, in which the pieces can be drawn twice in succession through the boiling water and beamed. The third bowl contains cold water. Of each pair of rollers, the lower one is driven by spur gearing, while the upper one can be raised or lowered at will for the purpose of decreasing or increasing the pressure.

Both tension and pressure are regulated by experience to suit the finish subsequently required.

Steaming.—In order to expose the pieces in the stretched condition to a higher temperature than they will be exposed to during any of the subsequent operations of dyeing and finishing, they are steamed. The last roller on which they are beamed in crabbing is a perforated iron cylinder. The outside of

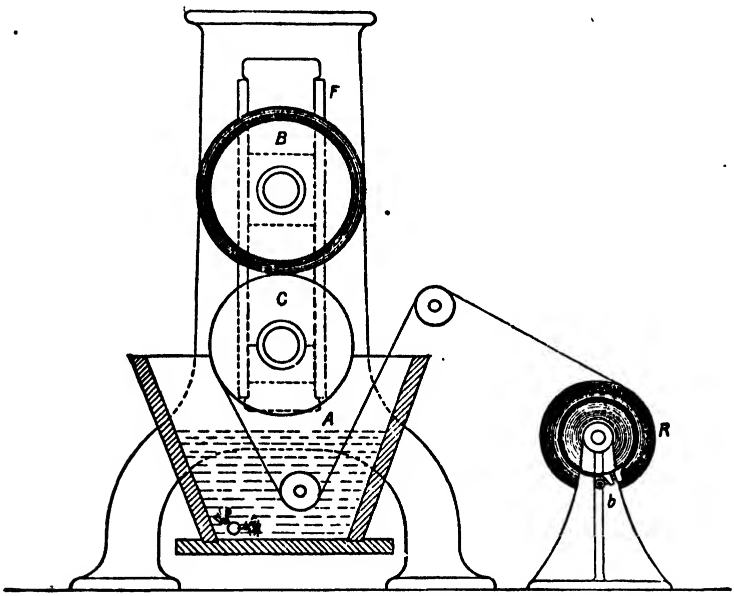


Fig. 47.—Single crabbing.

the pieces on the cylinder is enveloped in canvas, and steam at about 40 lbs. pressure is admitted through the bottom axis until it has traversed the whole thickness of the layer of material. After the first steaming, the pieces are allowed to cool, and are drawn under tension on to another perforated cylinder and steamed again. In this manner, those portions of the piece which were furthest away from the centre (where the temperature is greatest) come nearest the centre, and the effect of the steaming is more even. If this second steaming is omitted, the goods may become "ended," a fault which is due to the fact that high-pressure steam imparts to the wool an increased affinity for colouring matters. But, although twice steaming equalises to a large extent the effect of the steaming in this respect, those pieces which lie in the middle are necessarily exposed to a less severe action than the ends. It should be borne in mind that wool is easily affected by steam at high temperatures, and that too high a pressure in steaming may easily result in a tendering of the material.

The position of the cylinders in steaming may either be vertical or horizontal, but in both systems unevenness may result from condensation. This danger may be avoided in horizontal cylinders by causing them to revolve

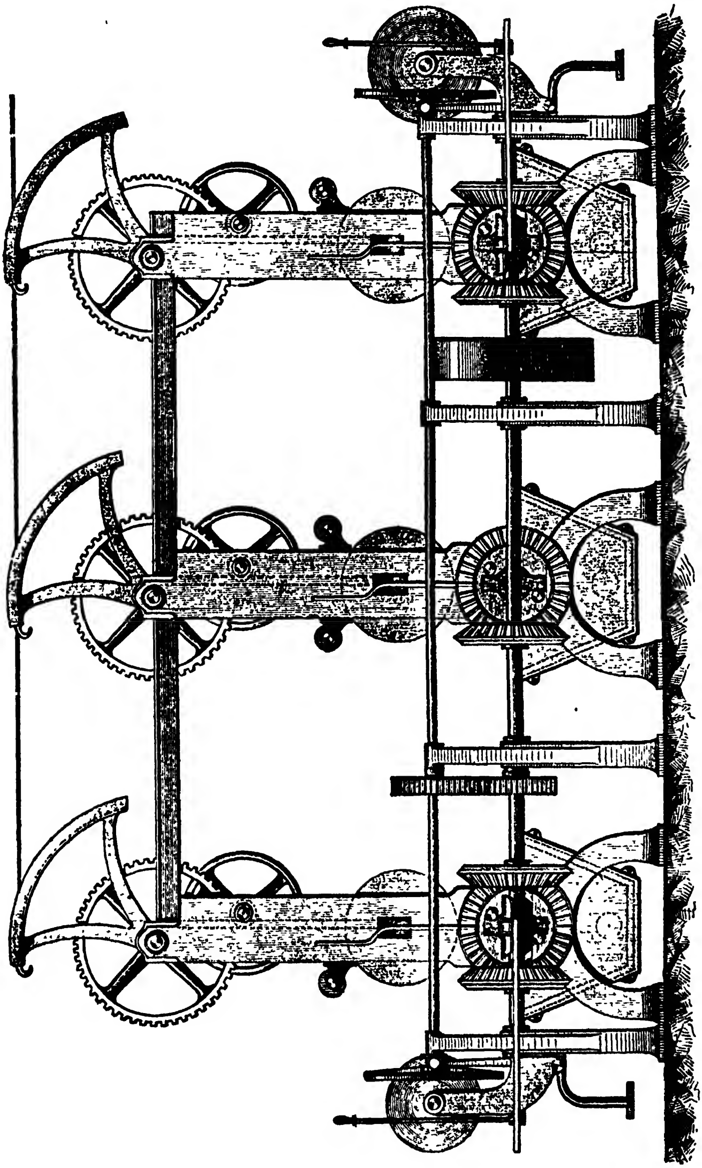


Fig. 48.—Treble crabbing machine.

slowly during the steaming. An arrangement of this kind, in which the steam may be caused to pass through from the centre or towards the centre, has been patented by Clay.*

* *Journ. Soc. Dyers and Col*, 1891, p. 159.

Fig. 49 is a longitudinal section of the machine, which comprises a box or chest, A, provided with a lid or cover, B, capable of opening upon hinges. As it is necessary for the box or chest to be steam- or air-tight, the lid, B, is hermetically sealed to the lower part of the chest by screws and nuts. The cloth or fabric to be treated is wound upon a perforated cylinder, M; the journal, N, of the cylinder is made hollow and is inserted into the tubular revolving shaft, O. The opposite end of the perforated cylinder is closed and provided with a cup, P, for receiving the centre, Q, which is made to move endwise to and from the cup by the hand wheel, R, after the manner of the spindle in a slide lathe. Each end of the box or chest is provided with stuffing boxes, S, which permit of the parts revolving whilst remaining steam-tight. The hollow revolving shaft, O, causes the perforated cylinder to revolve, the hollow shaft receiving its rotary motion by means of a worm wheel, T, gearing with a worm, U, driven by the driving pulleys, Y.

The *modus operandi* is as follows:—The hollow shaft, O, is placed in communication with a pump or exhaust fan, the result being that the air is drawn through the fabric, and through the perforated cylinder, passing away through the hollow shaft. When a vacuum has been thus formed, steam is introduced into the box through perforated pipes, W, and is drawn through

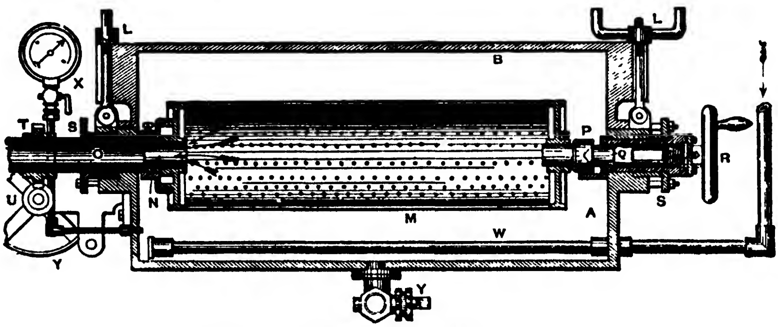


Fig. 49.—Clay's steaming arrangement.

the fabric by the exhausting fan or pump. The pressure of the steam within the chest is indicated on the steam gauge, X. The perforated cylinder continues to revolve during the steaming action, and the length of time the steaming is continued will depend upon the class of goods under operation, and the discretion and judgment of the operator. Y represents a valve for emptying the chest or box. Provision may be made for collecting the ejected liquid in any suitable form of receptacle, so that it may be re-used.

By a suitable arrangement of valves attached to the pump or fan, steam can be forced through the fabric in the reverse manner to that described, whereby both the inner and outer surfaces of the rolled fabric will be equally acted upon. Liquids may also be applied to the fabric in the same manner, and by connecting the valve, Y, to the pump or fan a complete circulation of the dye or other liquor is obtained.

After crabbing and steaming, the pieces are scoured previous to dyeing. The scouring is sometimes effected with advantage in the crabbing machine by substituting for the water in the first bowl a solution of soap or soda, or a mixture of both. This prevents the "setting" of the grease in the wool. When once "set," the grease is difficult to remove. No investigations appear to have been made for the purpose of investigating the cause of this fault.

Woollen goods are also frequently steamed, or crabbed and steamed, with the object of obtaining certain "finishes."

BLEACHING OF WOOL.

The method usually adopted for the bleaching of wool differs entirely from those used for the vegetable fibres. Indeed, were wool to be subjected to the same treatment as cotton, it would be completely dissolved in the first lime-boil. Nor has a treatment with chloride of lime any beneficial effect in removing the natural yellow colouring matter of the fibre.

The bleaching agent most usually employed is sulphurous acid, either gaseous or in solution as bisulphite, but generally gaseous. The operation of bleaching wool with gaseous sulphur dioxide is technically known as *stoving*.

Wool is sometimes bleached in the unmanufactured state (after washing and carbonising), also as slubbing, but generally either in the yarn or piece. Dyed yarns—*e.g.*, such as have been dyed with Rhodamine or Victoria blue—are sometimes stoved in order to brighten the shade.

For the stoving of worsted or woollen yarns, the hanks, after having been carefully scoured, are blued in a weak soap-bath containing a slight quantity of some such colouring matter as indigo carmine, Methyl violet, Methylene blue, &c., and are then hydro-extracted. They are then suspended on wooden rods and placed in the sulphur stoves, where they are exposed for six to eight hours, or over night, to an atmosphere of sulphurous acid produced by simply burning stick sulphur in the stove in an iron pot. The usual sulphur stove consists of a small brick or stone chamber, sometimes lined with wood, glass, or lead, 5 to 6 feet broad, 8 to 10 feet deep, and about 6 feet high. Care is taken in constructing such stoves to exclude all iron or other metals (wooden pegs being used in place of nails, &c.), since they would soon be destroyed by the acid atmosphere and might give rise to stains on the yarn. The average quantity of sulphur used is 6 to 7 lbs. for every 100 lbs. of wool.

When the operation is over, the doors of the stoves are opened, a draft of air is drawn through by removing the lid of an opening at the bottom end of the stove which is in connection with the works' chimney, and the yarn is taken out, aired, and dried.

For pieces the process is the same, but the construction of the stove is different. The pieces are sewn together, end to end, and pass through a narrow slit in the side of the stove, then many times up and down over wooden rollers, and ultimately out again at the same slit.

By stoving alone, it is not possible to obtain an absolutely pure white, a small amount of yellow still remaining in the material. The effect of this can be counteracted by blueing, which practically amounts to dyeing or tinting the wool with a colour complementary to the yellow, and thus producing an invisible grey. Bluish-violet dyestuffs yield the best results in this respect, but other dyestuffs, such as indigo extract, Alkali blue, Acid violet, Crystal violet, Light green, Victoria blue, and even Violamine, Rhodamine, and archil also find employment. Night blue and Lauth's violet have been found specially suited for the purpose. The yellow colour may also be to a large extent concealed by the use of white mineral colours, such as chalk, calcium sulphate, barium sulphate, or zinc white, and these, like the dyestuffs used for blueing, may either be applied before or after stoving. The following method of blueing piece goods after stoving is sometimes used :—

The pieces are first run in a dolly with water, until thoroughly wetted out, then run three times in succession in the same machine through freshly precipitated barium sulphate (prepared from 4 kilos. Glaubersalt and 3 kilos. barium chloride for every 100 kilos. of wool), along with the necessary amount of blue. The barium sulphate is taken up, along with the colouring matter, by the fibre. If the goods now match the pattern, they are washed, hydro-extracted, and dried.

The bleaching action of the sulphurous acid is quite different to that of chlorine. Some regard it as a reduction of the yellow colouring matter of the wool to a colourless leuco-compound, analogous to the reduction of Magenta to colourless leuco-rosaniline by passing sulphurous acid into the solution. By others it is supposed that the sulphurous acid combines chemically with the colouring matter, forming a colourless and soluble sulphurous acid compound, analogous to Alizarin blue S or Coeruleïn S (*q.v.*). That the change is not a permanent one is shown by the fact that stoved wool, if treated with alkalies like soap, again assumes its original yellow tinge.

Stoved wool tenaciously retains the sulphurous acid with which it has been treated. In stoved yarns, which are subsequently woven into coloured fancy fabrics, this fact is frequently a drawback, since the sulphurous acid in the stoved yarn may frequently bleach coloured yarns which cross it. In order to avoid this, G. Lunge recommends a treatment of the stoved yarn with peroxide of hydrogen by passing it through a dilute solution of this reagent. The sulphurous acid is thus rapidly and completely converted into sulphuric acid (which is harmless), while at the same time a further bleaching takes place.

In place of stoving, wool may be bleached by means of a solution of sulphurous acid or bisulphite of soda. In bleaching with sulphurous acid, the wool, previously well scoured, is steeped for twenty-four hours in a strong solution of sulphurous acid, wrung, and washed. For preparing the sulphurous acid solution, the liquefied sulphur dioxide, brought into the market in copper drums, is a convenient article. Free sulphurous acid has the disadvantage of injuring the health of the workpeople.

For bleaching with bisulphite of soda, Justinus Mullerus recommends the following process:—The scoured wool is steeped for twelve to fifteen hours in a solution of bisulphite of soda at 32° Tw., and after wringing, but without washing, it is passed through sulphuric acid at 6° Tw. Sulphurous acid is thus generated on and in the fibre.

A fairly good white may also be obtained by treating the wool for a half to two hours in a bath containing 20 to 30 per cent. sodium bisulphite, and 3 to 5 per cent. sulphuric acid (of the weight of the goods). After rinsing, the wool is blued with Methyl violet, Acid violet, or Fast acid violet in a warm soap-bath.

Bleaching of Wool with Hydrosulphite of Soda.—The bleaching agent first proposed for this purpose by F. V. Kallab* is prepared by gradually adding zinc powder to commercial bisulphite of soda diluted with about four times its bulk of water until no further reaction takes place. Milk of lime is then added in order to precipitate the zinc; and the clear supernatant liquid, which marks 1½° to 5° Tw., is used for bleaching. Small quantities of acetic acid and of finely-ground indigo are added to the bath. The latter serves for blueing, being reduced to indigo white, and acting as a dyestuff in spite of the bath not being alkaline (private communication from F. V. Kallab). The wool to be bleached is scoured and then immersed in the bleaching liquor for twelve to twenty-four hours. It is then taken out, washed in weak soda solution, then in water and exposed to the air, when the reduced indigo is oxidised on the fibre.

Bleaching of Wool with Hydrogen Peroxide and Sodium Peroxide.—This method is not very extensively used, owing to the expense of the bleaching agent, though it finds increasing application for high-class goods, since it yields a better and more permanent white than that obtained by stoving. Ebell† recommends the following process:—The wool is immersed in hydrogen peroxide of 3 per cent., to each litre (100 galls.) of which are added 20 c.c.

* See also Dommergue, *Journ. Soc. Dyers and Col.*, 1890, p. 111.
† *Journ. Soc. Dyers and Col.*, 1888, p. 29.

(2 galls.) ammonia (sp. gr. 0·910) and left at the ordinary temperature (12° to 17° C.) for twenty-four hours. If the temperature is raised to 30° C. the bleaching proceeds more rapidly, and is finished in eight to ten hours. Another method suggested is to steep the wool in the ammoniacal solution of hydrogen peroxide, wring it evenly, and dry in the air at the ordinary temperature. During the drying, the peroxide becomes concentrated on the fibre (according to Ebell) from a strength of 3 to 20 per cent., before an appreciable decomposition begins to take place, and it thus acts much more energetically.

According to H. Koechlin, wool pieces which have been previously well wetted-out are run through a mixture of hydrogen peroxide of 12 volumes' strength (1 vol.), water (1 vol.), and silicate of soda 32° Tw. ($\frac{1}{5}$ vol.), after which they are batched and allowed to lie for twenty-four hours, after which they are washed and dried. In another process recommended by Koechlin, the goods, after wetting-out and hydro-extracting, are run through hydrogen peroxide (1 vol.), water (1 vol.), and silicate of soda ($\frac{1}{20}$ vol.), steamed for two minutes, washed, and dried.

For bleaching with sodium peroxide, the wool is placed in a bath heated to 30° C., and containing 30 per cent. (of the weight of the wool) magnesium sulphate (free from chlorine), in which it is turned several times. The wool is then taken out, and 10 per cent sodium peroxide added to the bath, when the wool is re-entered and left in the bath for several hours. The bleaching action can be accelerated (1½ to 3 hours) by heating the bath to 50° to 60° C. The bleached material is washed in water containing sulphuric acid to remove the magnesia, and is then dried.

In place of using magnesium sulphate in preparing the bleaching bath, it is more economical to use sulphuric acid. For this purpose 3 parts by weight of sodium peroxide are dissolved in a cold solution of 4 parts sulphuric acid in a large excess of water. The solution is then tested with litmus, and exactly neutralised by the further addition of either acid or peroxide as may be found necessary. From 3 to 6 parts soluble glass 90° Tw. are then added. 100 lbs. wool require for bleaching about 10 lbs. sodium peroxide.

The bleaching effect of hydrogen peroxide is undoubtedly due to oxidation; but our knowledge of the reaction ends here, since we are unacquainted with the nature of the substances which it removes.

Bleaching of Woollen Pieces for Printing.—A common practice is to pass the pieces, after stoving, through chloride of lime acidulated with hydrochloric acid. This treatment destroys all the sulphurous acid retained by the fibre and chlorinates the wool, thus imparting to it a greater affinity for colouring matters.

H. Koechlin recommends the following process:—The pieces are drawn at full breadth through hydrogen peroxide of 12 volumes diluted with two to ten times its volume of water, according to the thickness of the material, the stronger bath being required for the denser textures. They are then squeezed batched on wooden rollers, and allowed to lie for twenty-four hours in this state. Then follows a treatment in bisulphite of soda at 64° Tw., also diluted with 2 to 10 parts of water. The pieces are beamed again and dried. They are then washed and chlorinated in a dolly with about 6 per cent. chloride of lime and excess of hydrochloric acid. After chlorinating they are washed and dried; and are then ready for printing.

Carbonising or Extracting.—It has already been pointed out (p. 134) that, in the condition in which it comes into the market, wool contains, in addition to suint and yolk, vegetable impurities (burrs) which cannot be entirely got rid of in washing. These burrs which cling to the fleece of the sheep are the fruits of plants (burr weeds) which represent principally different species of the genus *Xanthium* (nat. ord. Composites) or of *Medicago* * (nat. ord. Leguminous plants).

* The most commonly occurring is the *Medicago hispida* (Bathurst burr).

It is especially those belonging to the latter category (medicks) which, owing to their peculiar structure, it is impossible to entirely remove by combing, carding, or any other mechanical process. These burrs are almost invariably present in Botany wool, more especially in the better qualities. Fig. 50 shows the appearance of one of the three spiral parts of a fruit of this kind. When stretched out fully it measures nearly an inch in length.

The only radical means of getting rid of burrs is to destroy them by chemical means, and this is effected by carbonising, a process originally introduced during the fifties (by Gustav Köber). The same process serves for the destruction of vegetable fibres in woollen rags, previous to their being employed in the manufacture of shoddy and mungo.

The principle of carbonising lies in the application of solutions of certain mineral acids (or salts of such, which dissociate on heating) which, when concentrated on the material by drying, convert the cellulose into hydrocellulose. The latter crumbles to a powder or dust when rubbed, and is thus easily removed, while the wool suffers but little (if at all) by the treatment.

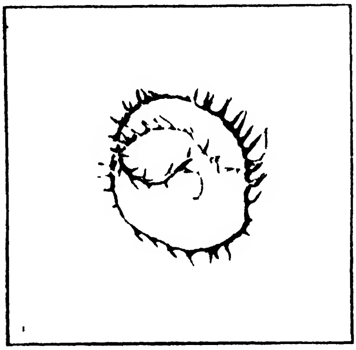


Fig. 50.—Single spiral of burr (Medick) × 2½ diameters.

Gauze patterns may also be obtained in fabrics by adopting the same principle, in the following manner:—The fabrics which are woven from union yarns (mixtures of cotton and wool) are printed with thickened aluminium chloride, and dried. The cotton is thus destroyed, leaving the wool, and that portion of the fabric is impoverished to such an extent as to represent only a gauze.

Carbonising Loose Wool.—In some cases the raw material is first washed with water only, then carbonised, and subsequently washed or scoured with soap. But, ordinarily, the scouring precedes the carbonising.

The scoured wool is first steeped for two to three hours in sulphuric acid at 5° to 6° Tw., allowed to drain, and hydro-extracted. The cage of the hydro-extractor should either be enamelled or covered with canvas to prevent iron stains. The removal of the excess of acid may also be effected by means of two pairs of squeezing rollers, the first being fluted, the second consisting of rollers of larger diameter, of which the lower one is covered with gutta-percha, while the upper one is of bronze. The wool thus treated is evenly spread on wooden lattice frames, of which several are placed on a framework running on wheels, and this latter is then pushed into the drying stove. The drying is first conducted in a current of air passed in from below at a temperature of about 55° C., and when no more moisture and acid vapours come off the air current is interrupted and the stove heated to 90° to 100° C. At this temperature the carbonising is rapidly effected.

The drying of the wool may also be effected on the counter-current principle in a machine which consists of a chamber in which are fitted travelling aprons of brass wire netting. The wool is fed in at the top, and is carried along to the end of the first travelling apron, where it drops on to the one immediately below it, and so on until, on arriving at the bottom of the chamber, it is seized by a pair of squeezing rollers, which eject it from the machine. The heating is effected by means of hot air from the flanged pipes, and the air (choosing the course of least resistance) is drawn up slowly by means of a fan in a direction contrary to that of the wool.

After drying or "baking," the wool is passed either through a willowing machine or through a burr-crushing machine similar to that shown in Fig. 51, with the object of removing the disintegrated burrs. The wool is conveyed by means of a lattice apron to the first pair of fluted rollers, and thence to the second, third, and fourth pairs of fluted rollers, each consecutive pair of rollers being driven at an accelerated speed as compared with the preceding ones, thus opening the wool gradually and laying bare the burrs, and crushing them whilst passing through. Close to the fourth pair of rollers is arranged a *batter* which beats the wool as it leaves these rollers, and so shakes it up that the

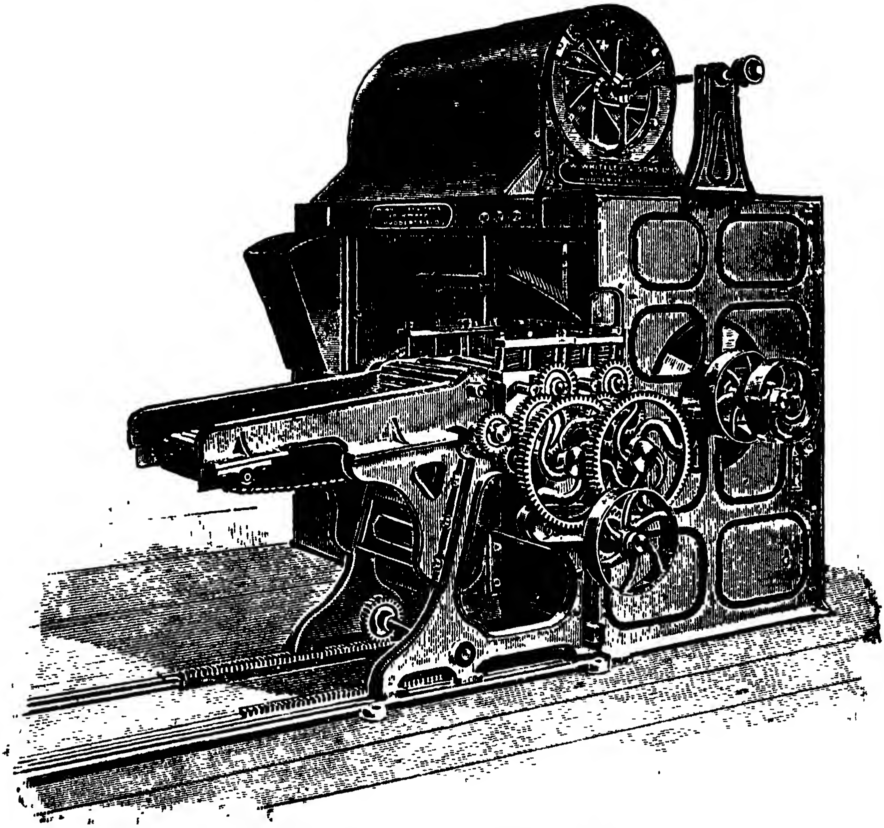


Fig. 51.—Burr-crushing machine (Whiteley & Sons, Ltd).

pulverised hydrocellulose is shaken out. The batter is enclosed in a perforated cage, to which an exhaust fan is attached, which withdraws all the dust and pulverised matter.

After this mechanical cleansing process, the acid remaining in the wool is removed or neutralised. This is effected by first washing in water, hydro-extracting, and then steeping in a solution of soda at 5° to 7° Tw. for about half an hour. It is then thoroughly washed in water. After washing, the wool should be tested to ascertain whether it still contains free acid, which is best done by means of blue litmus paper. This should not be reddened; on the other hand, although the wool should show a slight alkalinity, it should not give too pronounced a blue on red litmus paper. The incomplete removal

of the acid after carbonising may give rise to trouble in the subsequent operations, especially owing to the action of the acid on the metal parts of the preparing, carding, and spinning machinery. It should be noted that after carbonising wool has a greater affinity for colouring matters than before, and that consequently the two kinds cannot be used indiscriminately, as otherwise faults may occur after dyeing which are difficult to remedy.

Carbonising Wool in the Piece.—Wool is also carbonised in the piece, with the same object and by the same means as those which apply to the loose material. This practice has of late years been on the increase, the material being more conveniently dealt with in the piece than in the loose condition. Woollen cloth may be carbonised in the grey state—*i.e.*, just as it comes from the loom—and in this way the burrs are more completely removed than if the treatment is conducted after milling, cropping, raising, &c. On the other hand, the carbonising of woollen goods after these operations have been gone through offers the advantages of economy, and any deleterious action which the acid may exert on the milling properties of the fibre does not come into account. Piece goods may also be carbonised before dyeing, or between the operations of milling and raising, or lastly for whites and light colours before milling (so that the blackened burrs are completely removed). On the other hand, it is found advantageous, in many cases, to carbonise after dyeing, but since many colours, logwood especially, will not stand the action of sulphuric acid without being materially altered in shade, either aluminium chloride or magnesium chloride is frequently used in place of the acid. The action of these salts depends upon the fact that they are hydrolytically dissociated on drying, yielding free hydrochloric acid, which destroys the vegetable matter like sulphuric acid—

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl.$$
$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl.$$

The acid thus liberated has practically no effect on the colours, even logwood remaining unaffected, this being probably due to the presence in the fibre of an equivalent amount of base ($Al(OH)_3$ or $Mg(OH)_2$). Aluminium chloride is chiefly used for the purpose, since magnesium chloride, though considerably cheaper, requires a temperature (140° to 150° C.) to bring about its dissociation, at which the wool is liable to turn yellow. It gives, however, a harsh feel to the wool (see below), and is rather expensive; hence sulphuric acid is preferred whenever possible.

Carbonising with gaseous hydrochloric acid* is also employed, chiefly for woollen rags. This treatment also tends to destroy any silk which may be present.

Pieces to be carbonised must first be freed from grease by washing in soap, and the latter must be completely removed by subsequent washing in water. The goods are then steeped and slowly turned in the acid bath for about one to two hours. Sulphuric acid is used for this purpose at a strength of 6° to 9° Tw., while aluminium chloride should have a strength of 9° to 12° Tw., and magnesium chloride up to 15° Tw. When the acid has thoroughly penetrated into the material, the pieces are squeezed or hydro-extracted to remove excess of acid. In this condition the goods should not be allowed to lie for any length of time exposed to the air, otherwise they will dry in places, especially at the folds, and there become tender, while the wool in the tender places no longer possesses the same affinity for dyestuffs as the rest of the piece. This fault is erroneously supposed by some to be due to the action of light (especially direct sunlight), and for this reason the windows in the carbonising sheds are sometimes made of coloured glass.

* *Journ. Soc. Dyers and Col.*, 1885, p. 3.

The pieces are now dried, and this may be effected in various ways. The simplest method is to pass them over lapped drying cylinders, but this method is not largely adopted because of the damage which may thereby accrue to the cylinders and the harsh or "hask" feel which is imparted to the wool. Much better results are obtained by drying the pieces in a continuous drying stove, either in a current of hot air or by allowing them to pass in close proximity to steam-heated plates or pipes or over steam-heated cylinders. In one form of machine they pass up and down over rollers situated respectively at the top and bottom of the chamber, and leave the latter in the dry state. Steam-heated pipes run between the ascending and descending pieces all through the chamber. Another form of drying machine, which is largely used, consists of two horizontal drying chambers, in the first of which the pieces are dried in a current of air heated to between 55° and 65° C. Thence they pass into a second chamber, in which they are heated to between 90° and 110° C., which completes the carbonising. Care should be taken to prevent condensation in the drying chambers, since any drops which get into the pieces are liable to produce either thin places or holes.

According to circumstances, the goods are now either neutralised directly or they are first dry-milled in order to break up the burrs. This latter operation may be effected by running the goods dry for a short time through a dolly or milling machine. Then follows the removal of the acid. For goods which are subsequently to be dyed with acid colours, washing for twenty to thirty minutes in a dolly with water suffices, in case the dyestuff to be used has the property of dyeing level. But, if the dyestuffs do not possess this property, or the goods are subsequently to be dyed in the indigo vat or with mordant dyes, or have to be milled after carbonising, it is absolutely necessary that the acid should be carefully and completely neutralised. The neutralising is effected by running the goods first through water and then through soda in a dolly or broad washing machine, and then again through water. When aluminium chloride has been used for carbonising, the goods are liable to acquire a harsh feel in consequence of the deposition on the fibre of aluminium hydrate. Such goods are best washed first in pure water and then in water containing a small amount of sulphuric or hydrochloric acid, then again in water containing a little fuller's earth and soda.

DISCHARGING AND BLEACHING OF SILK.

Raw silk generally has a coarse appearance and a harsh feel; and is, consequently, seldom made use of for manufacturing purposes. In order to bring out its characteristic and valuable properties, it is necessary to remove the silk gum or sericine, which sticks the individual fibres together. The operation which is known as *ungumming* (Fr., *degommage*), *stripping*, or *discharging* may be effected in various ways, of which the following is the one most generally adopted. The process is generally carried out in two stages.

First Operation.—The hanks of silk suspended on wooden sticks are immersed in a soap solution contained in a rectangular wooden vat, the sides of which are covered with canvas. The soap usually employed for this purpose is a good neutral Marseilles or oleïn soap, and the amount taken varies from 20 to 35 per cent. of the weight of the silk. The temperature of the bath should be 90° to 95° C.; boiling must be avoided, since it would tend to entangle the silk and would cause the yellow colouring matter which is contained in some silks to become fixed on the fibre. The hanks are turned two or three times in the hot soap solution for one to one and a-half hours, during which the silk at first swells up considerably and becomes sticky; but,

as the sericine is dissolved off, the individual fibres begin to make their appearance and the silk becomes soft and glossy. For white silk or delicate colours, the boiling-off is preferably not done in one but in three separate baths, in each of which the hanks are turned for 20 to 30 minutes. As soon as the first bath has become charged with silk gum, it is emptied and filled with fresh soap solution and then serves as the last bath, and so on; so that a sort of counter-current is established, in which the fresh hanks are always treated with the soap solution which has been used twice over, while the last treatment is effected with fresh soap solution.

The thick waste liquor which comes from the last bath is a solution of sericine in soap, and is used as an addition to the dye-bath in dyeing silk with coal-tar colours, under the name of *boiled-off liquor*.

Soft water only should be used for boiling off, calcareous impurities being liable to mar the lustre of the silk. If none but hard water be available, it must be previously softened or corrected by suitable treatment, which will depend upon the nature of the hardness.

Many silks contain a small amount of lime in the sericine. To remove this, the hanks are steeped, before boiling-off, for a short time in dilute hydrochloric acid, after which they are washed and passed through a weak solution of soda crystals.

The boiled-off silk is rinsed in weak soda solution and wrung. At this stage it can be dyed in medium to dark colours, but if it is to be dyed white or in light colours, it is subjected to the next operation.

Second Operation.—The boiled-off hanks are tied loosely together with smooth tape, placed in coarse linen bags and boiled in round copper boilers for one-half to three hours, according to the quality of the silk, with 10 to 15 per cent. Marseilles soap. If the silk is not liable to become entangled, the bags may be dispensed with and the boiling done in open vessels, as in the first operation. The hanks are then taken out, rinsed in weak soda solution, then in running water, wrung evenly and dried.

The average loss in weight experienced in the boiling-off and discharging amounts to 25 to 30 per cent. for European, 18 to 22 per cent. for Japanese and Chinese silks.

Silk being an expensive article, such losses in weight materially affect the price of the finished article, and the dyer is frequently desired to reduce the loss to a minimum by means of a different mode of treatment.

Souple Silk is raw silk which has been treated in such a manner as to make it fit for dyeing, while the sericine is only partially removed.

1. *Scouring* (*dégraissage*).—The silk is turned for one to two hours in a solution containing 10 per cent. of soap at a temperature of 25° to 35° C. This treatment effects the removal of the fatty and wax-like impurities, and at the same time softens the fibre and causes it to swell. The operation is repeated.

2. *Bleaching* (*blanchiment*).—The scoured silk is turned for a quarter of an hour in a solution of aqua regia * at 3° to 4° Tw. Too long an immersion in the acid must be avoided, otherwise the silk is liable to be turned yellow by the nitric acid. In place of aqua regia, many dyers prefer a solution of "nitrose" (solution of nitrous acid in concentrated sulphuric acid) in water.

As soon as the silk has assumed a greenish-grey colour, it is taken out and washed well in water.

Stoving (*soufrage*).—The hanks are well and evenly wrung and exposed in sulphur stoves (see *Wool Bleaching*) for six to eight hours to an atmosphere

* The aqua regia is prepared by mixing 5 parts hydrochloric acid of 32° Tw. with 1 part nitric acid at 61° Tw.; and allowing the mixture to stand for four to five days at 28° C. It is then diluted down with water to the required strength.

of sulphurous acid. The operation is repeated several times according to the degree of white required. If the silk is to be subsequently dyed in dark shades, or blacks, this operation is omitted.

Soupling (*assouplissage*).—The object of this operation is to soften the silk which has become hard and brittle by the foregoing operations. It is softened by turning the hanks for about one and a-half hours in a solution of 3 to 4 grms. tartar per litre and washing, after this treatment, in warm water. In place of tartar, sodium bisulphate or magnesium sulphate and sulphuric acid may be employed.

Souple silk is not as strong as boiled-off silk, and is only used for weft. The loss in weight averages 6 to 8 per cent. It may be dyed in acid baths without any special precautions, but if dyed in soap-baths the temperature should not exceed 50° to 60° C.; otherwise the appearance of the silk suffers and a loss in weight results. For blacks the operations of bleaching and stoving are omitted.

Ecru Silk is raw silk which has been scoured in a weak soap solution to remove fatty and wax-like impurities, and then bleached by stoving. For blacks the stoving is omitted. The loss in weight amounts to 1 to 4 per cent. Ecru silk has a harsh feel, and is used for warp.

In case the raw silk is yellow, it is treated as follows:—Wet out twice with hot water, stove twice, wash and stove again twice or three times. If intended for white the following further treatments are required:—Wash cold with soap (1 lb. soap to 10 lbs. silk), rinse, stove twice, bleach with aqua regia or nitrose, rinse, treat in weak soda (2 ozs. soda to 10 lbs. silk), turn in a soap bath (4 ozs. soda to 10 lbs. silk), stove twice, and rinse in pure water or in water slightly acidulated with sulphuric acid.

Treatment with formaldehyde is now frequently used to fix the sericine (see p. 66).

In order to bring out to the fullest possible extent the characteristic and valuable properties of the fibre, discharged silk is subjected in the hank to the following mechanical operations:—

1. **Stretching** (*sécouage*).—This operation may take place before or after dyeing. The hanks are suspended on a stout, smooth, wooden peg, one end of which is fixed in the wall. By means of a smooth stick placed inside the hank, the operator stretches it by repeated jerks, the hank being turned on the peg from time to time. In this manner silk which has not been completely discharged may be stretched without disadvantage 2 to 3 per cent. in length. In order to save hand labour, the machine of C. Corron (Fig. 52) may be used for this purpose. The construction of the machine aims at an automatic imitation of the operation as carried out by hand. Four hanks are treated simultaneously, being suspended on the slowly rotating bobbins, A, while the stretching is effected by the intermittent raising and falling of the bars, B. Stretching is used largely for spun silk.

2. **Glossing** (*chevillage*).—The object of this operation is to increase the gloss of the fibre. This is sometimes done by hand by twisting the hanks very tight and allowing them to remain so for several hours. The operation is frequently repeated. The increased lustre is brought about by the friction of the fibres against each other.

But for this purpose, hand labour has been almost entirely superseded by machinery. Fig. 53 shows a silk glossing machine. The hanks are suspended on the bobbins, A. The bobbins, B, are inserted in the hanks and stretch the yarn by means of the heavy weights, *e*, to which they are attached. By means of an automatic arrangement, the bobbins, B, are turned two or three times round their axes, *c*, first to the right, then to the left, giving the hanks a sharp twist in each direction. After the bobbins, B, have

given the yarn two twists, once to the right and once to the left, they resume their original position. While they are temporarily at rest, the upper bobbins, A, turn slightly round, changing slightly the position of the hank, and the twisting goes on again; and so on until the required gloss has been obtained. Levers, *d*, are provided for lifting the heavy weights, in removing the hanks, and replacing them by fresh ones.

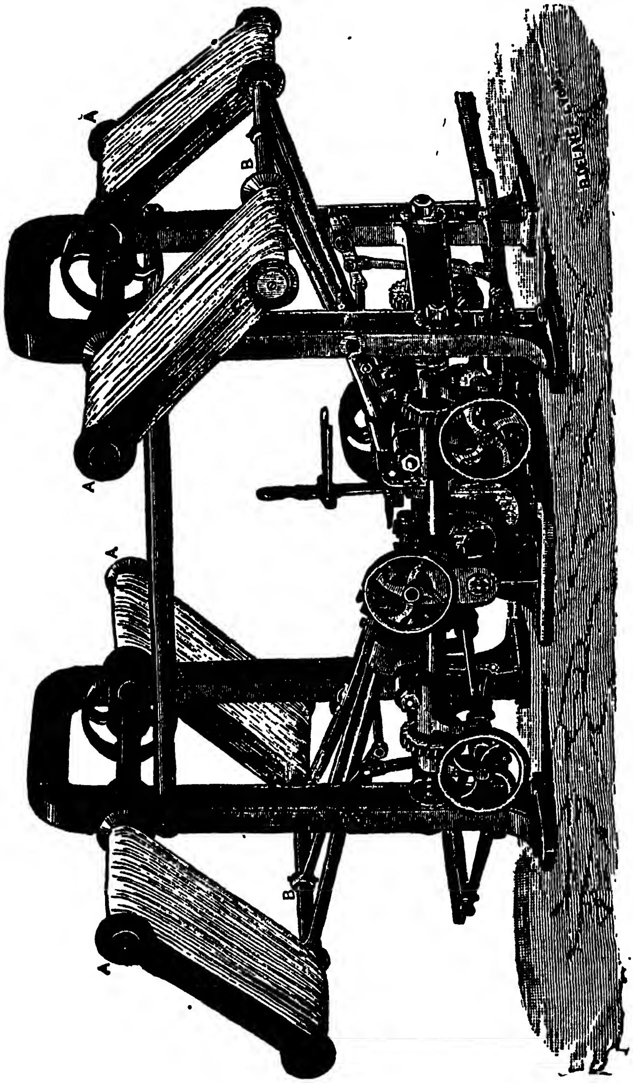


Fig. 52.—Corron's stretching machine.

The machine is also sometimes used for cotton yarn.

3. **Lustreing.**—The object of this operation is to impart to the silk the highest possible degree of lustre. This is effected by a simultaneous stretching and steaming in a machine like that shown in Fig. 54. The hanks are placed on the polished steel rollers, A and B; the lid is closed, steam is admitted

to the box, and the hanks subjected to tension by drawing back the roller, B, by means of the wheel, W. During the operation both rollers revolve in the

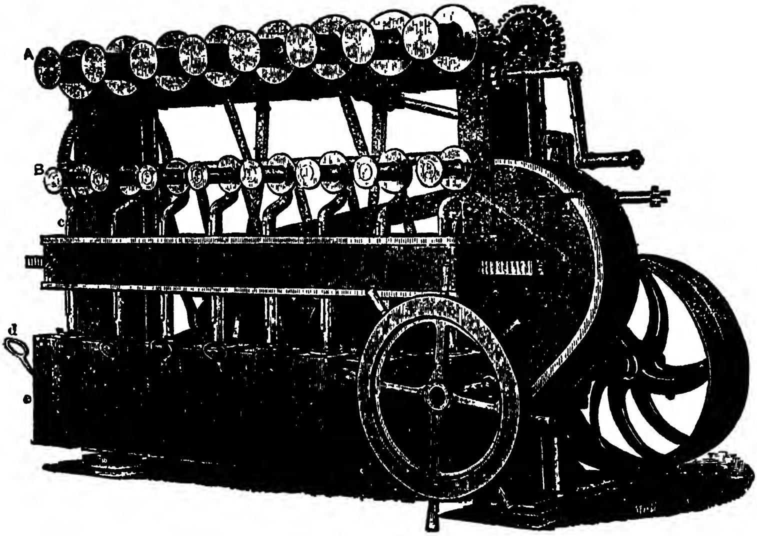


Fig. 53.—Silk glossing machine

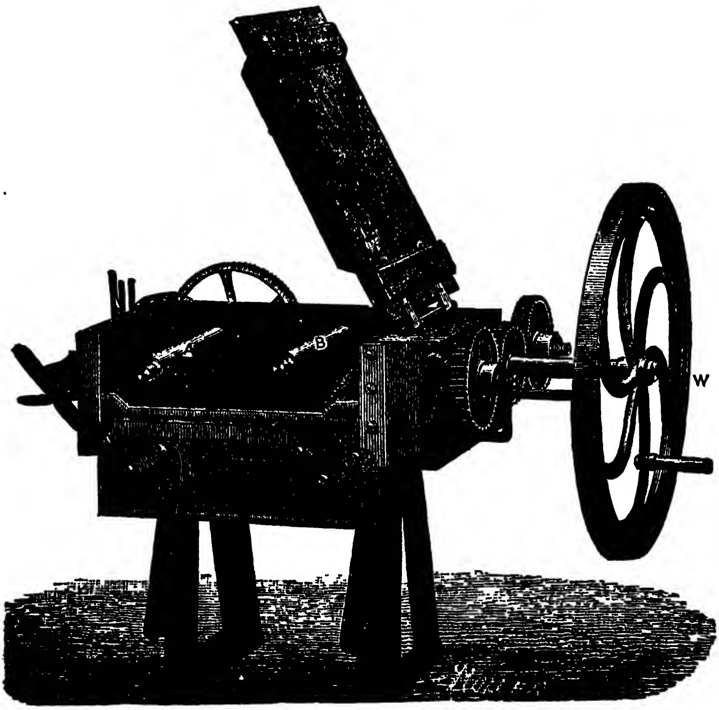


Fig. 54.—Silk lustreing machine.

same direction. One of the rollers is hollow and can be heated by steam and cooled again by circulating water.

In an improved machine by Burckhardt, in Basel, the steel rollers are cased in copper and are superposed. Both rollers are hollow, and can be heated or cooled by the admission of steam or water respectively. The tension is produced by hydraulic power, and more regular results are thus obtained than by hand-screw.

For ordinary purposes, the dyed hanks are stretched and steamed for half a minute under tension. The door is then opened, and the silk is allowed to cool and dry for about three minutes before being taken out.

With the object of obtaining an especially brilliant lustre (*teinture brilliant*), silk is subjected in the raw state to the following treatment:—Soak for two to twelve hours in lukewarm soap (20 to 30 per cent.), then wring and stretch wet (10 per cent.) for two minutes cold. After this treatment the hanks are boiled off in the ordinary way. The lustre may be still further increased by drying the hanks under slight tension on rods.

Silk lustred in this way is found to have lost nearly all its elasticity.

Discharging of Silk and Half-Silk Pieces.—Silk is sometimes discharged in the piece, with the object of facilitating the weaving, but more particularly in order to render possible the use of grège silk, which is not strong enough to withstand the strain in the loom after being discharged. The process of discharging is essentially the same as that used for hanks.

Piece goods consisting of wool and silk are usually first singed, crabbed, and steamed, and then discharged with soap and soda. The operation is best conducted on a jigger, care being taken to avoid creases, first with soap and soda at 40° C., then with soda alone at 50°, ultimately heating to the boil for a short time. Since wool is easily attacked by boiling aqueous alkalies, the ordinary process of discharging as used for all silk goods is not applicable to goods containing wool, as it would result in the more or less complete disintegration of this fibre. Hence, it is necessary to employ lower temperatures and to reduce the amount of alkali to a minimum.

According to another process, goods consisting of wool and silk are first treated with dilute hydrochloric acid and then discharged by heating for two to three hours to 90° C., after which they are lightly soaped and again steamed.

Pieces consisting of cotton and silk (satins, &c.) are treated like pure silk, since the cotton is not affected by the alkali. For the treatment, the pieces are frequently hooked in a spiral on to a frame such as is used in indigo dyeing (*q.v.*). For weighted coloured satins the goods may be treated first with tannin and then with stannic chloride, after which they are boiled off. In this way the silk is weighted and the cotton is at the same time mordanted for basic colours.

Bleaching of Silk.—Boiled-off silk is usually bleached like wool, with sulphurous acid (stoving). The stoving is repeated, however, in the case of silk from three to eight times, according to the quality of the silk, washing with water intervening between each stoving. Finally it is well washed in water and "dyed white" or tinted with various colours according to the desired shade.

Silk may also be bleached with liquid sulphurous acid or bisulphite of soda, but this method has not, according to M. Moyret,* met with success. On the other hand, the hydrosulphite process, as used for wool (see p. 150), has been successfully employed on silk. As in the case of wool, the effect of stoving is merely to decolourise by reduction (or formation of addition products) the natural colouring matter of the silk. Prolonged joint action of light and air consequently restores the original yellowish or brownish colour

* *Mon. de la Teint.*, 1891, p. 225.

of the fibre. Treatment of stoved silk with alkaline liquors also restores the natural colour more or less completely, a fact which must be taken into account if the material is to be dyed or tinted in an alkaline bath.

Yellow silk is best bleached by means of nitrous acid (sodium nitrite and hydrochloric acid).

Silk may also be bleached with hydrogen peroxide or sodium peroxide. The boiled-off silk is first treated with soap and ammonia, in order to remove any traces of fatty matter and to cause it to wet-out well. The bleaching proper is effected by one of the following processes:—

1. Into a wooden or earthenware vessel 10 volumes hydrogen peroxide (of 12 vols. strength) and 2 volumes ammonia (sp. gr. 0·910) are introduced, and the bath is heated to 25° to 30° C. In place of ammonia, borax, soluble glass, or magnesia may be employed for rendering the bath alkaline. The well-wrung silk is steeped in this bath and turned occasionally for twelve hours. If necessary, the process is repeated. After bleaching, the silk is dried slowly, preferably while being exposed as much as possible to light. Blueing is effected by treating the silk in a bath containing 30 per cent. soap and a small amount of a suitable colouring matter, such as Methyl violet. The effect of the soap is to restore the lustre of the silk which is lost in the bleaching process. Very good results are obtained, according to H. Koechlin, by the use of magnesia in place of ammonia, but at the finish it is necessary to acidulate the bath with sulphuric acid to dissolve the suspended magnesia and to thoroughly wash the silk afterwards.

2. Hydrogen peroxide (12 vols. strength) is diluted with three times its volume of water, and the solution rendered alkaline with ammonia, borax, soluble glass, or magnesia. The silk is steeped in this bath for one, two, or three days—according to the desired degree of bleaching—and is then rinsed and blued. It is not advisable to prolong the steeping over three days, since the fibre is liable to lose both strength and lustre.

3. Hydrogen peroxide (12 vols. strength) is let down with ten to twelve times its volume of water, and the solution rendered alkaline by the addition of borax, soluble glass, or magnesia. The silk is entered, turned for a quarter of an hour cold, when the bath is gradually heated to 90°, at which temperature silk is turned for three-quarters of an hour when it is taken out, rinsed, and blued.

Sodium peroxide can be used for bleaching silk as for wool (see p. 150), with this difference that the bath is heated for silk to 90° C. For a full bleach on 100 kilos. silk, about 12 kilos. sodium peroxide are necessary.

Silk may also be bleached with permanganate (like cotton or wool, *q.v.*), and this treatment is adapted for half-silk goods. Bleaching with electrolysed magnesium chloride solution is said to have given good results on a small scale.

TUSSUR SILK.

Tussur silk is ungummed or discharged like ordinary silk.

According to Silbermann, the following methods are commonly used for discharging Tussur silk:—

The silk is first scoured for half an hour at 40° C. in a bath containing 10 per cent. soda crystals, when it loses some 8 to 10 per cent. in weight. The bath is run to waste, as it cannot be used for fresh lots. After this treatment the silk is treated in a second bath containing 30 per cent. soda crystals for one to one and a quarter hours, first at 40° to 45° and ultimately at 90°. It is then rinsed and soured for ten minutes with 10 per cent. hydrochloric acid. Fine Tussurs are first scoured at 50° to 60° with 10 to 15 per cent. soda crystals, and

then boiled-off with 30 per cent. soap at 95° for three-quarters of an hour, after which they are treated with soda and rinsed in pure water, and may then be soured. The complete removal of the soap is of importance, since even traces remaining in the silk are apt to give it a grey colour. Tussur may also be boiled-off with 6 to 8 per cent. caustic soda at 60°. The operation lasts about half an hour, but care must be taken to prevent any attack of the fibre. If properly conducted, this method yields a silk possessing a high degree of lustre, the strength and elasticity being only slightly impaired. After discharging by one of the above processes, the Tussur should be soaped for half an hour, tepid, with 3 to 5 per cent. soap and then thoroughly rinsed. Ultimately it is soured hot in 10 per cent. hydrochloric or 5 per cent. hydrofluoric acid with the object of removing mineral constituents. By these treatments a further slight decrease in the tensile strength is brought about, which is more noticeable in silks containing much lime, but the lustre and elasticity increase.

After discharging, Tussur silk is not white, but of a brown colour, which cannot be got rid of by the ordinary process of stoving. The colour may be partially removed by a treatment in permanganate of potash and magnesium sulphate, followed by a bath of sulphurous acid.

Better results are said to be attained by the method proposed by Tessié du Motay, which consists in working the silk for about an hour in a bath heated to 90° C., and containing 50 to 100 per cent. barium peroxide on the weight of the silk. It is then passed through dilute hydrochloric acid, and washed.

The usual method of bleaching Tussur consists in boiling the silk with peroxide of hydrogen (100 per cent. of 10 volumes strength) and silicate of soda, which latter should be free from iron. It is not possible to bleach Tussur further than to a light cream, and some lustre is thus lost, but can be mostly restored by stretching. In consequence of the great degree of resistance which the fibre shows towards chemical reagents, more severe treatments might be employed with advantage for bleaching it than those usually suggested.

The following method has been proposed by Girard:—The silk is first treated with hydrochloric acid, then with a solution of soda or caustic soda at 3° Tw. The bleaching is then effected by steeping the silk for twenty-four hours in a weak solution of ammonium hypochlorite, prepared by double decomposition from bleaching-powder and ammonium carbonate or sulphate. The treatment with ammonium hypochlorite is repeated, if necessary. The silk is then passed through dilute hydrochloric acid, and washed.

PART V.

ACIDS, ALKALIES, MORDANTS, &c.

The drugs which are used by the dyer are, as a rule, divided into three groups:—

1. Chemicals generally.
2. Mordants.
3. Dyestuffs.

This division is based on the practical applications of the materials in question; but it is not correct, even from a merely practical point of view. Potassium bichromate, for example, which is generally called a mordant, acts as a dyestuff in the production of chrome yellow, and it might also be classed amongst the members of the first group, on account of its being used as an oxidising agent or for other purposes. It is still more difficult to give a theoretically satisfactory definition of the three groups.

Under *Chemicals* will be understood those materials which are employed in the preparing of the textile goods before dyeing—for instance, for bleaching—and which are required during the processes of dyeing and finishing, *without however, becoming part of the colour* either entirely or in part.

The character of the *Mordants* has been explained on p. 4, and, as stated there, they will be treated in this chapter together with the other chemicals, their application in mordanting and dyeing, however, will be dealt with under special headings.

The *Dyestuffs* will be treated in separate chapters (*q.v.*), since their chemical and tinctorial characters differ greatly from those of the other substances in use by the dyer.

ACIDS.

Sulphuric Acid (Oil of Vitriol), $H_2SO_4 = SO_2(OH)_2$.—Sulphuric acid is produced on the large scale by allowing sulphur dioxide, nitrous gases, air, and aqueous vapour to react on each other in leaden chambers. The nitrous fumes simply act as carriers of oxygen, and the process may be considered to take place according to the following equations:—

$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO.$$
$$NO + O = NO_2$$

The acid which collects in the chambers is known as *chamber acid*, and has a specific gravity of 1·54 to 1·60 By further concentration in leaden pans, or in the Glover-tower, a brown coloured acid with a specific gravity of 1·69 to 1·73 and a strength of 76 to 80 per cent. H_2SO_4 is obtained, which is known as *brown oil of vitriol* (B.O.V.). This acid is further concentrated in vessels of glass, platinum, or iron, and thus the commercial *concentrated sulphuric acid* or *oil of vitriol* (O.V. or D.O.V.—*i.e.*, double O.V.) is produced; this product contains, however, 3 to 5 per cent., and even as much as 7 per cent., water. Stronger acid, corresponding to the formula H_2SO_4 (the so-called *monohydrate*), is obtained by mixing the commercial article with sulphur trioxide (fuming

sulphuric acid). Recently the catalytic or contact process has been introduced in various places. It consists in condensing dry sulphur dioxide and oxygen at an elevated temperature by the action of finely-divided platinum or ferric oxide (burnt pyrites), the resulting sulphur trioxide being converted according to requirements into sulphuric acid.

Sulphuric acid is a thick oily liquid without colour or smell, which possesses a specific gravity of about 1·838 at 15°, and boils at 338°; it begins, however, to distil at 290°, and is thereby partially decomposed into sulphur trioxide and water. The acid becomes solid below 0°, and melts again at 10·5°.

Sulphuric acid absorbs water with great avidity and with evolution of great heat. The greatest care has to be observed in mixing it with water that it does not boil up; *water should never be poured into strong sulphuric acid; the acid should always be allowed to flow into the water slowly and in a thin stream with stirring, and even then the water must not be hot.* Sulphuric acid which has been diluted with half its weight of water does not give off great heat on being further diluted. The acid may absorb moisture from the air, and, by increasing in volume, may overflow the vessels in which it is contained, but when it is diluted with water, the resulting volume of the mixture is less than the sum of the volumes of the acid and water before mixing (measured at the same temperature). The mixture undergoes contraction, and the contraction is greatest when the liquids are in the proportion of one molecule of acid to two molecules of water.

Sulphuric acid is, under ordinary conditions, the strongest acid we possess. It forms salts with all metals, and displaces, in most cases, other acids which are combined with bases. It is a dibasic acid, and forms either neutral salts like Na_2SO_4, or acid salts like $NaHSO_4$. The salts of sulphuric acid are called the *sulphates*; the acid salts are known as *bisulphates* or *acid sulphates*. Sulphuric acid dissolves most of the metals; it either forms salts with them, as is, for instance, the case when the dilute acid acts on iron or zinc, hydrogen being evolved—$H_2SO_4 + Fe = FeSO_4 + H_2$; or it dissolves the metal by a complicated process, when a part of the acid is reduced to sulphurous acid, which escapes, while no hydrogen is liberated; this is the case when the strong hot acid acts on copper—$2H_2SO_4 + Cu = CuSO_4 + SO_2 + 2H_2O$. Iron is dissolved by diluted sulphuric acid, but an acid of 1·65 specific gravity or more has no effect on this metal at the ordinary temperature, and very little at elevated temperatures; hence strong acid can be further concentrated or transported in iron vessels; hence, too, many chemical processes in which sulphuric acid is used are effected in iron vessels.

PERCENTAGE AND SPECIFIC GRAVITY OF SULPHURIC ACID AT 15° C. (*Otto*).

Per cent. by Weight. H_2SO_4.	Specific Gravity.	Per cent. by Weight. SO_3.	Per cent by Weight. H_2SO_4.	Specific Gravity.	Per cent. by Weight. SO_3.	Per cent. by Weight. H_2SO_4.	Specific Gravity.	Per cent. by Weight. SO_3.
1	1·0064	0·816	11	1·0756	8·980	21	1·1516	17·14
2	1·0130	1·630	12	1·0830	9·790	22	1·1590	17·95
3	1·0190	2·445	13	1·0910	10·61	23	1·1670	18·77
4	1·0256	3·260	14	1·0980	11·42	24	1·1740	19·58
5	1·0320	4·080	15	1·1060	12·24	25	1·1820	20·40
6	1·0390	4·890	16	1·1136	13·06	26	1·1900	21·22
7	1·0464	5·710	17	1·1210	13·87	27	1·1980	22·03
8	1·0536	6·530	18	1·1290	14·69	28	1·2066	22·85
9	1·0610	7·340	19	1·1360	15·51	29	1·2150	23·67
10	1·0680	8·160	20	1·1440	16·32	30	1·2230	24·49

Sulphuric acid extracts the elements of water from many substances; thus many organic compounds—*e.g.*, sugar, starch, or vegetable fibres—are entirely decomposed and charred (*carbonised*), while others are otherwise chemically changed.

SPECIFIC GRAVITY OF SULPHURIC ACID AT 60° F. (15$\frac{5}{9}$° C.)
(*Lunge and Isler*).

Degrees Twaddle.	100 Parts by Weight contain		Kilo. per Litre. H_2SO_4.	Degrees Twaddle.	100 Parts by Weight contain		Kilo. per Litre. H_2SO_4.	Degrees Twaddle.	100 Parts by Weight contain		Kilo. per Litre. H_2SO_4.
	SO_3.	H_2SO_4.			SO_3.	H_2SO_4.			SO_3.	H_2SO_4.	
40	22·30	27·32	0·328	86	43·36	53·11	0·759	132	60·11	73·64	1·222
41	22·82	27·95	0·337	87	43·75	53·59	0·769	133	60·46	74·07	1·233
42	23·33	28·58	0·346	88	44·14	54·07	0·779	134	60·82	74·51	1·244
43	23·84	29·21	0·355	89	44·53	54·55	0 789	135	61 20	74·97	1·256
44	24·36	29·84	0·364	90	44·92	55·03	0·798	136	61·57	75·42	1·267
45	24·88	30·48	0·373	91	45·31	55·50	0·808	137	61·93	75·86	1·278
46	25 39	31·11	0·382	92	45 69	55·97	0·817	138	62·29	76·30	1·289
47	25·88	31·70	0·391	93	46·07	56·43	0·827	139	62·64	76·73	1·301
48	26·35	32·28	0·400	94	46·45	56·90	0·837	140	63·00	77·17	1·312
49	26·83	32·86	0·409	95	46·83	57·37	0·846	141	63·35	77·60	1 323
50	27·29	33·43	0·418	96	47·21	57·83	0·856	142	63·70	78·04	1·334
51	27·76	34·00	0 426	97	47·57	58·28	0·866	143	64·07	78·48	1 346
52	28·22	34·57	0·435	98	47·95	58·74	0·876	144	64·43	78·92	1·357
53	28·69	35·14	0·444	99	48·34	59·22	0 886	145	64·78	79·36	1·369
54	29·15	35·71	0·454	100	48·73	59·70	0·896	146	65·14	79·80	1·381
55	29·62	36·29	0·462	101	49·12	60·18	0·906	147	65·50	80·24	1·392
56	30·10	36·87	0·472	102	49·51	60·65	0·916	148	65·86	80·68	1·404
57	30·57	37·45	0·481	103	49·89	61·12	0·926	149	66·22	81·12	1·416
58	31·04	38·03	0·490	104	50·28	61·59	0·936	150	66·58	81·56	1·427
59	31·52	38·61	0 500	105	50·66	62·06	0·946	151	66·94	82·00	1·439
60	31·99	39·19	0·510	106	51·04	62·53	0·957	152	67·30	82·44	1 451
61	32·46	39·77	0·519	107	51·43	63·00	0·967	153	67·65	82·88	1·463
62	32 94	40·35	0·529	108	51·78	63·43	0·977	154	68·02	83·32	1·475
63	33·41	40 93	0·538	109	52·12	63·85	0·987	155	68·49	83·90	1·489
64	33·88	41·50	0·548	110	52·46	64·26	0·996	156	68·98	84·50	1·504
65	34·35	42·08	0·557	111	52·79	64·67	1·006	157	69·47	85·10	1·519
66	34·80	42·66	0·567	112	53·12	65·08	1·015	158	69·96	85·70	1·534
67	35·27	43·20	0·577	113	53·46	65·49	1·025	159	70·45	86·30	1·549
68	35·71	43·74	0·586	114	53·80	65·90	1·035	160	70·94	86·90	1·564
69	36·14	44·28	0·596	115	54·13	66·30	1·044	161	71·50	87·60	1·581
70	36·58	44·82	0·605	116	54·46	66·71	1·054	162	72·08	88·30	1·598
71	37·02	45·35	0·614	117	54·80	67·13	1·064	163	72 69	89·05	1·621
72	37·45	45·88	0·624	118	55·18	67·59	1·075	164	73·51	90·05	1·639
73	37·89	46·41	0·633	119	55·55	68·05	1 085	165	74 29	91·00	1·661
74	38·32	46 94	0 643	120	55·93	68·51	1·096	166	75·19	92·10	1·685
75	38·75	47·47	0·653	121	56·30	68 97	1·107	167	76·27	93·43	1·713
76	39 18	48·00	0·662	122	56·68	69·43	1·118	$167\frac{6}{10}$	77·23	94·60	1·739
77	39 62	48·53	0·672	123	57·05	69·89	1·128	$167\frac{8}{10}$	77·55	95·00	1·748
78	40·05	49·06	0·682	124	57·40	70·32	1·139	168	78·04	95·60	1·759
79	40·48	49·59	0·692	125	57 75	70·74	1·150	$168\frac{2}{10}$	79 19	97·00	1·786
80	40·91	50·11	0·702	126	58·09	71·16	1·160	$168\frac{3}{10}$	79·76	97·70	1·799
81	41·33	50·63	0 711	127	58·43	71·57	1·170	$168\frac{2}{10}$	80·16	98·20	1·808
82	41·76	51·15	0·721	128	58·77	71·99	1·181	168	80·98	99·20	1·825
83	42·17	51 66	0·730	129	59·10	72·40	1·192	$167\frac{8}{10}$	81·39	99·70	1·834
84	42·57	52·15	0·740	130	59·45	72·82	1·202	$167\frac{7}{10}$	81·59	99·95	1·838
85	42·96	52·63	0·750	131	59·78	73·23	1 212				

The number of pounds of H_2SO_4 per gallon is found by multiplying the number in the fourth column by 10 (Kilo. per Litre).

Commercial sulphuric acid contains both a varying amount of water and several other impurities, notably arsenic, selenium, lead, iron, sulphur dioxide, or nitrous gases. In addition, the acid is often coloured by organic dust which has been charred by the liquid. The commercial product, however, is usually pure enough for the requirements of the dyer.

In this book the term "sulphuric acid" will, unless otherwise indicated, refer to the concentrated acid of 168° Tw.

The strength of sulphuric acid is determined by titration with normal alkali (see under *Analysis*). For an approximate estimation it is sufficient to ascertain the specific gravity with a hydrometer. Sulphuric acid of 98 per cent. H_2SO_4 possesses the highest specific gravity; the density of the liquid decreases on further concentration, and the monohydrate shows about the same density as an acid containing 95 per cent. H_2SO_4.

Sulphuric acid is the most important of all chemical products, and is manufactured on an enormous scale. It may be said that our whole civilisation is dependent on this substance; most chemical industries and many other trades use it extensively; in the production of dyestuffs and other materials which are indispensable in dyeing, it cannot be replaced. It is used in bleaching, mordanting, and dyeing, for the carbonising of woollen materials, &c.

Fuming or *Nordhausen sulphuric acid* is sulphuric acid containing varying quantities of *sulphur trioxide* or *sulphuric anhydride*, SO_3 in solution.

Sulphur Dioxide, SO_2.—Sulphur dioxide is the product of the combustion of sulphur. It is produced on the large scale by burning sulphur or sulphur ores; in the laboratory from sulphuric acid by heating the latter with charcoal, sulphur, or copper turnings. Sulphur dioxide is a colourless gas, possessing the characteristic suffocating smell of burning sulphur; it is 2·21 times heavier than air, and can be reduced by cold (–15° C.) or by pressure (30 lbs. per sq. in.) to a colourless liquid which boils at 8° C. It is brought into commerce in this liquefied form, which is very convenient for use in the laboratory. Sulphur dioxide is very soluble in water; the saturated solution contains per volume—

At	0° : 68·86	volumes	SO_2,	specific gravity	1·061.
,,	10° : 51·38	,,	SO_2,	,,	1·055.
,,	20° : 36·21	,,	SO_2,	,,	1·024.

The solution of the gas in water may be considered to contain *sulphurous acid*, H_2SO_3.

Sulphur dioxide does not sustain respiration; neither animals nor plants can live in an atmosphere containing comparatively small amounts of the gas. It does not support combustion, and hence, is sometimes used in extinguishing fires.

Sulphur dioxide has considerable affinity for oxygen, combining with it in the free state with the aid of finely-divided platinum at high temperatures (as in the catalytic process for manufacturing sulphuric anhydride, see p. 164). The solution of the gas slowly absorbs oxygen from the air, and forms sulphuric acid. Sulphur dioxide is also oxidised by compounds that contain much oxygen; bichromate of potash, for instance, is converted into chromium sulphate, and permanganate into manganous sulphate. On the other hand, it is reduced to sulphur by sulphuretted hydrogen, $SO_2 + 2SH_2 = 3S + 2H_2O$.

Sulphur dioxide possesses in the presence of water reducing properties, of which use is made in bleaching. According to the equation, $SO_2 + 2H_2O = H_2SO_4 + H_2$, hydrogen is liberated, in presence of many coloured organic compounds, which are thereby transformed into colourless soluble substances. Since the latter oxidise in the air and regenerate the

original colouring matter, washing must follow the bleaching to remove these substances entirely. Thus sulphur dioxide is used in gaseous form and in solution for bleaching wool and silk, straw, feathers, &c.; bisulphites are applied in a similar way.

Sulphurous Acid, $H_2SO_3 = SO(OH)_2$, which is known only in solutions, is the hydrate of sulphur dioxide. It is a dibasic acid, and forms neutral salts or *sulphites*, like Na_2SO_3, and acid salts or *bisulphites*, like $NaHSO_3$. *Metasulphite* (or pyrosulphite) of potassium and of sodium contains one equivalent of water less than the corresponding bisulphite, $Na_2S_2O_5 = 2NaHSO_3 - H_2O$.

Hydrochloric Acid, HCl (*Muriatic acid; spirits of salt*).—Hydrochloric acid is obtained by the decomposition of sodium chloride (common salt) with sulphuric acid according to the equation—$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$. Enormous quantities are produced in this way as a bye-product in the manufacture of soda by the "Le Blanc process."

In the pure state, hydrochloric gas is a colourless gas which fumes strongly in moist air, has a penetrating smell, and dissolves readily in water.

Hydrochloric acid (*i.e.*, the aqueous solution) when pure is a colourless liquid. The most concentrated acid has, at 15° C., the specific gravity of 1·212, and contains 43 per cent. hydrochloric acid gas, some of which is gradually given off into the atmosphere with the evolution of white fumes. When distilled, it loses gas until it is diluted to a certain strength that varies with the pressure. At the ordinary atmospheric pressure, a liquid distils which boils at a constant temperature of 110°, has the specific gravity 1·101, and contains 20·2 per cent. (by weight) of hydrochloric acid gas.

SPECIFIC GRAVITY OF HYDROCHLORIC ACID AT 15°C., COMPARED WITH WATER AT 4°C. AND REDUCED TO VACUUM.
(*Lunge and Marchlewsky*).

Degrees Twaddle.	Specific Gravity at $\frac{15°}{4°}$ in vacuo.	100 Parts by weight contain parts by weight of HCl.	1 Litre contains grms. HCl.*	Degrees Twaddle.	Specific Gravity at $\frac{15°}{4°}$ in vacuo.	100 Parts by weight contain parts by weight of HCl.	1 Litre contains grms. HCl.*
0	1·000	0·16	1·6	21	1·105	20·97	232
1	1·005	1·15	12	22	1·110	21·92	243
2	1·010	2·14	22	23	1·115	22·86	255
3	1·015	3·12	32	24	1·120	23·82	267
4	1·020	4·13	42	25	1·125	24·78	278
5	1·025	5·15	53	26	1·130	25·75	291
6	1 030	6·15	64	27	1·135	26·70	303
7	1·035	7·15	74	28	1·140	27·66	315
8	1·040	8·16	85	29	1·145	28·61	328
9	1·045	9·15	96	30	1·150	29 57	340
10	1·050	10·17	107	31	1·154	30·55	353
11	1·055	11·18	118	32	1·160	31·52	366
12	1·060	12·19	129	33	1·165	32·49	379
13	1·065	13·19	141	34	1·170	33·46	392
14	1·070	14·17	152	35	1·175	34·42	404
15	1·075	15·16	163	36	1·180	35·39	418
16	1·080	16·15	174	37	1·185	36·31	430
17	1·085	17·13	186	38	1·190	37·23	443
18	1·090	18·11	197	39	1·195	38·16	456
19	1·095	19·06	209	40	1·200	39·11	469
20	1·100	20·01	220				

* The number of pounds HCl contained in a gallon is found by dividing the number in the fourth column (grms. HCl per litre) by 100. It may be noticed that each degree Twaddle indicates approximately 1 per cent. HCl.

Hydrochloric acid is one of the strongest acids, and replaces most other acids in their compounds. It is a monobasic acid, and forms salts which are called *chlorides*—*e.g.*, sodium chloride, NaCl. Most of these salts are readily soluble in water. Hydrochloric acid dissolves many metals with evolution of hydrogen, and dissolves most metallic oxides and hydroxides. Lead is attacked by hot hydrochloric acid; hence lead-lined vessels and leaden pipes cannot be used in working with this acid. Hydrochloric acid is oxidised by the higher oxides, such as manganese dioxide, lead dioxide, nitric or chromic acid, &c., the hydrogen combining with oxygen to form water, and chlorine being liberated; on this fact depend both the process of producing chlorine from the acid with the aid of manganese dioxide and the energetic action of *aqua regia*.

Commercial hydrochloric acid contains iron, arsenic, sulphuric acid, and organic matter, and has a yellow colour; it is generally pure enough for technical purposes. The commercial product has a specific gravity of 1·12 to 1·19 (24° to 38° Tw.); it is shipped in glass carboys, or in large earthenware pots.

The strength of hydrochloric acid is determined by acidimetric titration (see under *Analysis*), or, roughly, by the hydrometer, the specific gravity increasing with the strength (see table on p. 167). Hydrochloric acid is, next to sulphuric acid and soda, the most important chemical product. It is not used extensively in the dye-house, but it can be employed in many cases when sulphuric acid is used. It is used in great quantities for the preparation of dyer's materials.

Nitric Acid, $HNO_3 = NO_2(OH)$.—Nitric acid is manufactured by the decomposition of sodium nitrate by sulphuric acid—$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4$. It is a colourless liquid possessing a slight smell, and fumes strongly in the air. It has a specific gravity of 1·53, and boils at 86° with partial decomposition into nitrogen peroxide, oxygen, and water; acid containing 32 per cent. water (sp. gr. 1·414) boils without decomposition. Nitric acid is a very strong monobasic acid, the salts of which are known as *nitrates*. It dissolves most metals, thereby forming salts which are generally soluble in water; during the reaction, a part of the acid is generally reduced to lower oxides of nitrogen and even to elementary nitrogen and ammonia. Iron is not attacked by concentrated nitric acid, but moderately diluted nitric acid (of a sp. gr. above 1·12) dissolves it to ferric nitrate, while a weaker acid forms ferrous nitrate and ammonium nitrate.

Nitric acid is a powerful oxidising agent, and many organic substances are ignited when moistened with the same—*e.g.*, straw and sawdust—while some almost explode in contact with the same—*e.g.*, alcohol and turpentine. The concentrated acid is also extremely corrosive to the skin, and may produce deep and painful wounds; the diluted acid colours the skin, wool, silk, feathers, and many other organic substances yellow.

Commercial nitric acid contains lower oxides of nitrogen, by which it is coloured slightly yellow, and, in addition, small amounts of chlorine and iodine, which were present in the nitrate, as also iron, sulphuric acid, and sodium nitrate and sulphate. The strength varies from 1·35 to 1·44 specific gravity.

Aqua fortis is impure nitric acid which contains a considerable amount of the lower oxides of nitrogen. The ordinary commercial nitric acid is also frequently called aqua fortis.

The strength of nitric acid is determined by acidimetric titration or by the hydrometer.

SPECIFIC GRAVITY OF NITRIC ACID AT 15°C., COMPARED WITH WATER OF 4°C. AND REDUCED TO VACUUM (*Lunge and Rey*).

Degrees Twaddle.	Per cent. HNO_3 by weight.	Degrees Twaddle.	Per cent HNO_3 by weight.	Degrees Twaddle.	Per cent. HNO_3 by weight.	Degrees Twaddle.	Per cent. HNO_3 by weight.	Degrees Twaddle.	Per cent. HNO_3 by weight.
0	0·10	21	17·89	42	33·82	63	49·89	84	69·80
1	1·00	22	18·67	43	34·55	64	50·71	85	70·98
2	1·90	23	19·45	44	35·28	65	51·53	86	72·17
3	2·80	24	20·23	45	36·03	66	52·37	87	73·39
4	3·70	25	21·00	46	36·78	67	53·22	88	74·68
5	4·60	26	21·77	47	37·53	68	54·07	89	75·98
6	5·50	27	22·54	48	38·29	69	54·93	90	77·28
7	6·38	28	23·31	49	39·05	70	55·79	91	78·60
8	7·26	29	24·08	50	39·82	71	56·66	92	79·98
9	8·13	30	24·84	51	40·58	72	57·57	93	81·42
10	8·99	31	25·60	52	41·34	73	58·48	94	82 90
11	9·84	32	26·36	53	42·10	74	59·39	95	84·45
12	10·68	33	27·12	54	42·87	75	60·30	96	86·05
13	11·51	34	27·88	55	43·64	76	61·27	97	87·70
14	12·33	35	28·63	56	44·41	77	62·24	98	89·60
15	13·15	36	29·38	57	45·18	78	63·23	99	91·60
16	13·95	37	30·13	58	45·95	79	64·25	100	94·09
17	14·74	38	30·88	59	46·72	80	65·30	101	96·39
18	15·33	39	31·62	60	47·49	81	66 40	102	98·10
19	16·32	40	32·36	61	48·26	82	67·50	103	99 07
20	17·11	41	33·09	62	49·07	83	68·63	104	99·67

Nitric acid finds an extensive application in the arts; for example, in the production of sulphuric acid, nitroglycerin, and most artificial dyestuffs. Dyers do not use it much in the free state, except for the preparation of certain mordants; but salts and other products of nitric acid are of great importance in the dye-house.

Formic Acid, CH_2O_2 = HCO(OH).—Formic acid occurs in the bodies of ants, stinging nettles, muscles, and in the human or animal perspiration. It is produced at the Nitrite Works of Coepenick, near Berlin, by the action of carbon monoxide on caustic soda or on the alkaline earth bases at high temperatures and under high pressure, and is supplied to the trade in various grades of strength up to nearly 100 per cent.

Formic acid is a colourless liquid, which possesses a pungent smell, and produces blisters on the skin. It melts at 8·6° C., and boils without being decomposed at 100·8° C. Its specific gravity at 19·8° C. is 1·2201. It mixes with water and with alcohol in all proportions. Owing to the aldehydic group it contains, formic acid is a powerful reducing agent; it converts, *e.g.*, chromic acid into chromium oxide. Formic acid is a well-defined monobasic acid, the salts of which are called *formates*. All normal formates are soluble in water.

Formic acid has come into use as a substitute for acetic acid or sulphuric acid in dyeing wool with acid colours. Its action in causing the exhaustion of the acid dye-bath is two or three times as strong as that of acetic acid, and nearly as strong as that of sulphuric acid. Compared with the latter it offers the great advantage that it does not tender cotton, but it is much more expensive, and does not fix the acid colours on wool quite as fast to washing. Formic acid brings about the complete exhaustion of the chrome bath in chroming wool, and is, therefore, used as an assistant for chroming. It has also been recommended as a substitute for hydrochloric, tartaric, and other acids in dyeing Aniline black, in order to avoid all risk of tendering. For leather dyeing and deliming it has also proved extremely useful.*

* A. G. Green and A. B. Stevens, *Journ. Soc. Dyers and Col.*, 1904, p. 6; S. Kapff, *ibid.*, 1905, p. 75.

Acetic Acid, $C_2H_4O_2$ = $CH_3CO(OH)$.—*Glacial Acetic Acid—Pyroligneous Acid—Vinegar.*—Acetic acid is produced by the destructive distillation of wood, and by the acetous fermentation of alcohol and alcoholic liquors (beer, wine, &c.). The pure concentrated acid is called glacial acetic acid, because it solidifies when cooled, thereby forming an ice-like mass. It is produced from pure acetates (obtained from wood-tar). Pyroligneous acid is a crude acetic acid obtained by neutralising wood-tar with lime, and decomposing the resulting salt with sulphuric acid. Vinegar, finally, is the product of acetous fermentation of alcoholic liquids.

Pure acetic acid (glacial acetic acid) is a colourless substance which possesses a penetrating acid smell, and a strong acid taste. It forms a crystalline mass of 1·105 specific gravity, which melts at 17° C., and boils without being decomposed at 118° C. It is hygroscopic, and mixes with water and with alcohol in all proportions; in mixing with water contraction and increase of specific gravity take place; a mixture containing 77 per cent. acetic acid and 23 per cent. water, corresponding to the formula $C_2H_4O_2 + H_2O$, has the highest specific gravity (1·075 at 15·5°); while a mixture of about equal weights of acid and water has the same specific gravity as the pure acid. In determining the concentration of strong acid with the hydrometer, this fact must be taken into account. Acetic acid is a well-defined monobasic acid, the salts of which are called *acetates*. All normal acetates are soluble in water.

SPECIFIC GRAVITY OF ACETIC ACID AT 15° C. (*Oudemans*).

Specific Gravity.	Per Cent. $C_2H_4O_2$.	Specific Gravity.	Per Cent. $C_2H_4O_2$.	Specific Gravity.	Per Cent. $C_2H_4O_2$.	Specific Gravity.	Per Cent. $C_2H_4O_2$.
0·9992	0	1·0363	26	1·0631	52	1·0748	77
1·0007	1	1·0375	27	1·0638	53	1·0748	78
1·0022	2	1·0388	28	1·0646	54	1·0748	79
1·0037	3	1·0400	29	1·0653	55	1·0748	80
1·0052	4	1·0412	30	1·0660	56	1·0747	81
1·0067	5	1·0424	31	1·0666	57	1·0746	82
1·0083	6	1·0436	32	1·0673	58	1·0744	83
1·0098	7	1 0447	33	1·0679	59	1·0742	84
1·0113	8	1·0459	34	1·0685	60	1·0739	85
1·0127	9	1·0470	35	1·0691	61	1·0736	86
1·0142	10	1·0481	36	1·0697	62	1·0731	87
1·0157	11	1·0492	37	1·0702	63	1·0726	88
1·0171	12	1·0502	38	1·0707	64	1·0720	89
1·0185	13	1·0513	39	1·0712	65	1·0713	90
1·0200	14	1·0523	40	1·0717	66	1·0705	91
1·0214	15	1·0533	41	1·0721	67	1·0696	92
1·0228	16	1·0543	42	1·0725	68	1·0686	93
1·0242	17	1·0552	43	1·0729	69	1·0674	94
1·0256	18	1·0562	44	1·0733	70	1·0660	95
1·0270	19	1·0571	45	1·0737	71	1·0644	96
1·0284	20	1·0580	46	1·0740	72	1·0625	97
1·0298	21	1·0589	47	1·0742	73	1·0604	98
1·0311	22	1·0598	48	1·0744	74	1·0580	99
1·0324	23	1·0607	49	1·0746	75	1·0553	100
1·0337	24	1·0615	50	1·0747	76		
1·0350	25	1·0623	51				

Note.—The specific gravities above 1·0553 correspond to two liquids of different strength. To find whether a certain solution contains more or less than 77 per cent. $C_2H_4O_2$ (which mixture possesses the highest specific gravity) a little water may be added; if the specific gravity increases, the acid was above 77 per cent., otherwise below this strength.

Concentrated acetic acid dissolves many organic substances, also sulphur and phosphorus. The acid neutralises basic oxides completely, but it does not prevent or affect many chemical processes, as the strong inorganic acids and oxalic acid do; further, it does not attack the vegetable fibre, either in solutions or on drying. For these reasons acetic acid is largely used in dyeing.

Commercial Acetic Acid. — Pure glacial acetic acid is chiefly used for scientific or pharmaceutical purposes. Diluted, more or less, impure acetic acid, produced from acetate of lime, is used for technical purposes. It contains generally about 29 per cent. $C_2H_4O_2$, and possesses a specific gravity of 1·04 (= 8° Tw.); the impurities of this acid consist chiefly of empyreumatic substances, but should not contain any free sulphuric or other mineral acid. The data in this book refer to the commercial acetic acid of 29 per cent. $C_2H_4O_2$.

Pyroligneous acid contains considerably more empyreumatic substances than the previous article, and these exert a strong reducing action (they decolourise potassium permanganate). The pyroligneous acid is preferable for its reducing power in many cases, as, for instance, for the preparation of pyrolignite of iron, because it prevents a premature oxidation of the iron, for which reason it is frequently employed instead of the purer commercial product (see under *Analysis*).

The hydrometer cannot be used with advantage for the estimation of acetic acid; for a reliable valuation the acidimetric titration is necessary.

Oxalic Acid, $H_2C_2O_4 = \left\{ \begin{matrix} CO(OH) \\ CO(OH) \end{matrix} \right.$.—Oxalic acid is manufactured by heating sawdust with caustic potash and soda; it can be obtained by the oxidation of many organic substances, and occurs in the juice of many plants in the form of potassium- and calcium-salts.

Oxalic acid crystallises in prisms which have the composition $H_2C_2O_4 + 2H_2O$; the crystals lose their water of crystallisation at 100° C. It can be sublimated by careful heating to 150° to 160° C., and is decomposed by higher temperatures. The crystals dissolve at ordinary temperatures in about eight times their weight of water (see table below); at 90° they dissolve in one-third their weight of water. The acid is not acted upon by nitric acid or chlorine, but it is oxidised by potassium permanganate, and by manganese peroxide in acid solution forming carbon dioxide.

Oxalic acid is a strong dibasic acid, and forms neutral salts, so-called *oxalates*, and acid salts or *binoxalates*. The alkaline oxalates are soluble in water; most of the other oxalates are insoluble. The neutral oxalate of calcium is insoluble both in water and in acetic or oxalic acid, but readily soluble in hydrochloric or nitric acid.

Oxalic acid and the oxalates are poisonous. The commercial article is nearly pure acid. The acid is estimated by acidimetric or oxidimetric (permanganate) titration (see under *Analysis*).

Oxalic acid is used largely in dyeing.

SPECIFIC GRAVITY OF SOLUTIONS OF OXALIC ACID,
$H_2C_2O_4 + 2H_2O$ at 15° (*Franz*).

Specific Gravity.	Per Cent. $H_2C_2O_4+2H_2O$.	Specific Gravity.	Per Cent. $H_2C_2O_4+2H_2O$.	Specific Gravity.	Per Cent. $H_2C_2O_4+2H_2O$.
1·0032	1	1·0182	6	1·0271	10
1·0064	2	1·0204	7	1·0289	11
1·0096	3	1·0226	8	1·0309	12
1·0128	4	1·0248	9	1·0320	12·6
1·0160	5				

Tartaric Acid, $C_4H_6O_6 = \left\{\begin{array}{l} CO(OH) \\ CH(OH) \\ CH(OH) \\ CO(OH) \end{array}\right.$—*Ordinary Tartaric Acid, Dextro-tartaric Acid.*—Tartaric acid exists both in the free state and in the form of salts in the juice of many fruits (grapes), and is deposited as acid potassium salt or tartar during the fermentation of wine; the acid is obtained from the crude tartar.

Tartaric acid forms large transparent prisms of strong and pure acid taste, which melt at 170° C., and are decomposed by higher temperatures without distilling; it is easily soluble in water, but less so in alcohol. Tartaric acid is a strong dibasic acid; its salts are known as *tartrates.* The commercial article is nearly pure; it contains some sulphuric acid, lime, and other metallic oxides.

Tartaric acid is estimated by acidimetric titration (see under *Analysis*).

SPECIFIC GRAVITY OF TARTARIC ACID SOLUTIONS AT 15° C. (*Gerlach*).

Specific Gravity.	Per Cent. $C_4H_6O_6$.	Specific Gravity.	Per Cent. $C_4H_6O_6$.	Specific Gravity.	Per Cent. $C_4H_6O_6$.
1·0045	1	1·0969	20	1·2078	40
1·0090	2	1·1072	22	1·2198	42
1·0179	4	1·1175	24	1·2317	44
1·0273	6	1·1282	26	1·2441	46
1·0371	8	1·1393	28	1·2568	48
1·0469	10	1·1505	30	1·2696	50
1·0565	12	1·1615	32	1·2828	52
1·0661	14	1·1726	34	1·2961	54
1·0761	16	1·1840	36	1·3093	56
1·0865	18	1·1959	38	1·3220	(saturated) 57·9

Tartaric acid is frequently employed in dyeing and printing, both in the free state and in the form of the potassium salt (tartar). It is chiefly used as an addition to the mordant bath in wool dyeing and for brightening colours on silk after dyeing, as also as a resist and discharge in printing.

Citric Acid, $C_6H_8O_7 = C_3H_4(OH)(CO_2H)_3$.—Citric acid exists in the juice of lemons, limes, oranges, and other fruits; it is obtained from the juice of lemons (or lime-fruit) which comes into commerce from southern Europe and the West Indies.

Citric acid crystallises in prisms with one molecule of water of crystallisation, $H_8C_6O_7 + H_2O$, which melt at 153° C.; it dissolves in three-quarters its weight of water at 15° C. and in twice its weight of alcohol.

Citric acid is a well-defined tribasic acid; the salts are known as *citrates.*

Commercial citric acid consists of large crystals which often show a yellowish tinge but do not contain any considerable quantity of impurities. A good acid should leave no ash when incinerated.

Citric acid is estimated by titration or by taking the specific gravity of its aqueous solution. It is used as a resist and discharge in printing.

Lactic Acid, $C_3H_6O_3 = CH_3CH(OH)CO_2H$ (*Ordinary* or *Ethylidene Lactic Acid*).—Lactic acid is generated by the so-called lactic fermentation of various kinds of sugar (cane sugar, sugar of milk, &c.) in the presence of albuminoid substances, especially of caseïn; it occurs in sour milk, and is now produced on a large scale at a cheap price. If distilled at 15 mm. pressure it boils with little decomposition at 122° C., the evaporated acid of 99 per cent. yielding a hard crystalline mass, which melts at 18° C. It partially evaporates with

aqueous vapours, and it mixes in all proportions with water or alcohol, but is not freely soluble in ether.

Commercial lactic acid forms a yellowish or brown syrupy liquid of 1·178 specific gravity (or more) at 15° C., which should contain 50 per cent. (by weight) of pure lactic acid, and usually contains some sulphuric acid, sugar, dextrine, iron, and other impurities. Lactic acid of 70 per cent. strength is also now in the market.

Lactic acid is a weak monobasic acid, the salts of which are known as *lactates*. Most of the salts are soluble in hot or cold water, but only sparingly so in alcohol, and not soluble in ether. Lactoline is said to be an acid potassium lactate, and is used as an assistant for mordanting wool.

Lactic acid has been used for some time for mordanting wool with potassium bichromate as a substitute for tartar on account of its greater reducing power, and has been generally recommended as a substitute for tartaric and other organic acids in dyeing and printing, for which purposes its mild acidity is in some cases beneficial, in others detrimental. Its hygroscopicity is a disadvantage in cotton-printing, but may act usefully in silk- and wool-printing. A double lactate of antimony and calcium is used under the name of *antimonine* as a substitute for tartar emetic, and some other lactates have also been recommended for various purposes.

Laevulinic Acid, $C_5H_8O_3 = CH_3COCH_2CH_2CO_2H$.—Laevulinic acid is produced by the action of acids on cane sugar, laevulose, cellulose, starch, and other carbohydrates.

Laevulinic acid crystallises in scales which melt at 33° and boil at 239° C. It is very soluble in water and in alcohol. It is a monobasic acid.

At the present time laevulinic acid is used to a limited extent in calico printing, its employment as a solvent for induline having been patented by the Hoechst Colour Works. It may possibly replace oxalic, tartaric, and citric acid in many cases.

OIL-MORDANTS.

Higher Fatty Acids (Fatty Oils, Fats, &c.).

Palmitic Acid, $C_{16}H_{32}O_2 = C_{15}H_{31}(CO \,.\, OH)$, is a white substance which melts at 62° C., and can be distilled under diminished pressure without being decomposed. It is a monobasic acid, the salts of which are called *palmitates*. Potassium and sodium palmitates are the chief constituents of palm oil soap; they are decomposed by water (see *Soap*). The other salts are insoluble in water.

Palmitin or *Tripalmitin*, $(C_{16}H_{31}O_2)_3C_3H_5$, is the glycerin ether of palmitic acid. It occurs in most animal fats, in olive oil and in palm oil, and melts at 66° C. Palmitin is decomposed into glycerin and palmitic acid, or a palmitate, on being heated with sulphuric acid, alkalies, lime, or superheated steam. The process of decomposition with alkali of this and similar ethers is called *saponification*, and the resulting salt *soap* (see below). Palmitic acid is used by dyers in the form of soap.

Stearic Acid, $C_{18}H_{36}O_2 = C_{17}H_{35}(CO \,.\, OH)$.—Stearic acid closely resembles palmitic acid. It is a white substance which melts at 69° C., and can be distilled under diminished pressure without being decomposed. It is a monobasic acid, and its salts are called *stearates*. These salts have the same properties as the palmitates.

Stearin or *Tristearin*, $(C_{18}H_{35}O_2)_3C_3H_5$, the glycerin ether, melts at 72° C., and yields the acid by saponification. Stearin occurs in all solid animal fats, and is best prepared from mutton-fat or shea-butter.

Stearic acid is one of the chief constituents of ordinary soap.

Oleïc Acid, $C_{18}H_{34}O_2 = C_{17}H_{33}(CO.OH)$.—Oleïc acid is obtained as a bye-product in the manufacture of stearic acid, and can be prepared by saponification of oleïn, its glycerin ether, which is the chief constituent of olive oil. Oleïc acid is a colourless oil which melts at 14° C., but which cannot be volatilised without undergoing decomposition. It is a monobasic acid, and forms salts which are called *oleates* and resemble the palmitates and stearates.

Oleïc acid contains two atoms of hydrogen less than stearic acid, and can be converted into this compound by the action of hydrogen in the nascent state, $C_{18}H_{34}O_2 + 2H = C_{18}H_{36}O_2$. It readily takes up two atoms of iodine or bromine and forms di-iod- or dibrom-stearic acid; for instance $C_{18}H_{34}O_2 + I_2 = C_{18}H_{34}I_2O_2$. By oxidation with potassium permanganate in alkaline solution it is transformed into dioxystearic acid, $C_{18}H_{34}(OH)_2CO_2H$. While in the pure state it possesses neither colour, taste, nor smell, and does not act on litmus; by the oxidising action of the air it turns yellow, and acquires a rancid smell. It possesses in an eminent degree the property of absorbing oxygen. According to Camille Koechlin, oleïc acid takes up under the influence of light 300 to 400 times its volume of oxygen from the atmosphere. Oleïc acid is converted by nitrous acid into the isomeric *elaïdic* acid, $C_{18}H_{34}O_2$, which melts at 45° C. Oleïc acid in form of the sodium or potassium salt is a constituent of many soaps, especially of olive-oil soap. In the form of oleïn it is a very important material for the production of Turkey red.

Oleïn or *Trioleïn*, $(C_{18}H_{33}O_2)_3C_3H_5$, the glycerin ether of oleïc acid, is present in most fatty oils, and forms, as already stated, the chief constituent of olive oil. It melts at − 6° C.

The glycerin ethers of palmitic, stearic, and oleïc acids are the chief constituents of most animal and vegetable fats and fatty oils—in contrast with the ethereal oils. As oleïn is a liquid, while palmitin and stearin are solid, the fluidity or hardness of such fatty oils and fats depends upon the larger or smaller percentage of oleïn they contain. These glycerin ethers cannot be distilled without undergoing decomposition whereby the glycerin is converted into acroleïn, C_3H_4O, a volatile liquid possessing a powerful penetrating smell (the smell of burnt fat). The fats are resolved into the corresponding acids and glycerin when heated with very dilute sulphuric acid, caustic alkalies, or alkaline earths, and by the action of steam; even by the action of moist air they are partially decomposed in this way, thus becoming "rancid." The alkali-salts of these acids form the essential constituents of soap, and for this reason the process of splitting fats into acids and glycerin by alkalies and by other agents is called "saponification." The lead salts of these three acids are obtained by boiling fats with lead oxide and water; they are not soluble in water, and are called "lead plasters."

The fatty oils are separated into the drying and non-drying oils; the drying oils differing from the others in becoming dry and resinous from oxidation in the air or from polymerisation. This change depends upon the presence of glycerides of oleïc and similar acids—*i.e.*, acids which contain less than twice as many atoms of hydrogen as of carbon. Many drying oils contain the glycerin ether of *linoleïc acid*, $C_{16}H_{28}O_2$. The different kinds of *wax* are related to the fats, being ethers of fatty acids and of monovalent higher alcohols; *beeswax*, for instance, consists essentially of the palmitic ether of melissyl alcohol, $C_{30}H_{62}O$.

Ricinoleïc Acid (*Oxyoleïc acid*), $C_{18}H_{34}O_3 = C_{17}H_{32}(OH)(CO_2H)$, is a white crystalline mass which melts at 16° to 17° C. The glycerin ether, *ricinoleïn*, $(C_{18}H_{33}O_3)_3C_3H_5$, is the chief constituent of castor oil, and yields the acid on saponification.

Ricinoleïc acid takes up two equivalents of hydrogen, bromine, or iodine, &c., analogously to oleïc acid. Both acids are unsaturated compounds, and

possess in a high degree the property of becoming polymerised, thereby forming compounds of a greater molecular weight. The products of polymerisation play an important part in the production of Turkey red, and will be referred to again.

Ricinoleïc acid is an oxyoleic acid, and differs from oleïc acid in its behaviour towards sulphuric acid. Ricinoleïc acid probably forms a true sulphuric ether by actual etherification, whereas oleic acid is not etherified in the usual way, although it probably also yields a true sulphate (see below).

Turkey-red Oil, Alizarin Oil, Sulphated Oil, Soluble Oil or Oleïn.—These names apply to products which are obtained by the action of sulphuric acid on vegetable oils at the ordinary temperature. Olive oil, cotton-seed oil, and possibly some other oils are used to some extent, but castor oil alone is the most important raw material used in the preparation of the sulphated oil of the cotton dyer and printer The process of manufacture, as it takes place on the large scale, has been described by various writers * in conformance with other reports. Castor oil is slowly and thoroughly mixed (from 12 to 24 hours) with the proper quantity of concentrated sulphuric acid, the temperature not being allowed to rise above 40° C. Sulphuric acid, to the extent of from 10 to 40 per cent. of the weight of the oil, is used, in winter more acid being required than in summer. The mixture is allowed to stand until a sample poured into distilled water yields a clear solution, when it must be washed at once, as the product readily decomposes. The product is washed with a solution of common salt, or Glauber's salt, to remove the excess of free acid, and it is finally partially neutralised and diluted to the required strength. During the treatment with sulphuric acid the heat is not allowed to rise too high, otherwise the evolution of considerable quantities of sulphur dioxide takes place, and a dark coloured product is obtained, which gives unsatisfactory results in dyeing. But in any case some sulphur dioxide is perceived by its smell, which probably results from the decomposition of the albuminoids and other extraneous matter in the oil. Soda or ammonia is used for neutralising, and the oil is diluted with water, so as to make a finished product containing 45 to 50 per cent. fatty matter (unless it is kept stronger to save expense of freight). J. A. Wilson gives the following average composition:—

20 to 27	per cent.	free fatty acids,
25	,,	combined acid and glycerides,
1·30 to 1·50	,,	Na_2O.

Fremy was the first who studied the action of sulphuric acid on fatty oils in detail; and Runge (*Farben Chemie*, 1834) recognised already the value of the sulphated olive oil, and recommended its employment in dyeing.† The firm of Gros, Roman, Marozeau & Co., in Wesserling, employed the product during the early sixties for the fixation of aniline dyestuffs; and, later, it was also used for goods to be printed with Alizarin (*E. Lauber*, *H. Schmid*).‡ The processes remained secret, and the results were not quite satisfactory, since the goods acquired a yellowish tint on steaming, which could not be removed by bleaching. The introduction of sulphated castor oil was a great improvement, and this article is now used almost exclusively for Turkey-reds, Alizarin-reds, and print goods (except in the production of Turkey-reds by means of rancid Gallipoli oil). Sulphated castor oil was brought into the market (almost simultaneously) by an English and a French firm. In 1876 John M. Sumner &

* J. A. Wilson, *Journ. Soc. Dyers and Col.*, 1891, p. 94; P. Lochtin, *ibid.*, 1890, p. 82.

† The firm Braun & Cordier, in Rouen, used as early as 1846 a product which was obtained by the action of nitric acid on olive oil for the preparation of cotton for Turkey-reds. The process was invented by Hirn. (Persoz, *Traité d'Impression*; Henri Schmid, *Dingler's Polyt. Journ.*, 250, p. 543.)

‡ *Dingler's Polyt. Journ.*, 247, p. 11; *ib.*, 250, p. 543.

Co., of Manchester, introduced the sodium salt of sulphated castor oil, invented by Dr. Wuth in Ramsbottom; and P. L'Honoré, of Havre, manufactured the corresponding ammonium salt discovered by Fr. Storck. A. Mueller-Jacobs manufactured sulphated castor oil at an early date in Russia, and claims to have taken part in the discovery.* The composition of sulphated oil has been the object of several investigations, and is now fairly clear.

The first detailed publication was made by Liechti and Suida.† According to these authors a compound ether of the oil and sulphuric acid is formed, having the following constitution—

$$\left.\begin{matrix} C_{18}H_{33}O_3 \\ SO_4 \\ C_{18}H_{33}O_3 \end{matrix}\right\} \begin{matrix} C_3H_5OH \\ \\ C_3H_5OH \end{matrix} \qquad \text{and} \qquad \left.\begin{matrix} C_{18}H_{33}O_5 \\ SO_4 \\ C_{18}H_{33}O_5 \end{matrix}\right\} \begin{matrix} C_3H_5OH \\ \\ C_3H_5OH \end{matrix}$$

from *olive oil.* from *castor oil.*

while oxidised acids are also obtained—viz., from olive oil or oleïc acid, $C_{18}H_{34}O_3$, and from castor oil or ricinoleïc acid, $C_{18}H_{34}O_5$.

The oxygen required for the production of such oxyacids was furnished by the reduction of sulphuric acid to sulphur dioxide, a considerable amount of which escaped during the process. Since in the production of commercial sulphated oil the evolution of sulphur dioxide is strenuously avoided, Liechti and Suida's researches do not perfectly explain the usual process.

R. Benedict‡ prepared the true sulphonic acid of a higher fatty acid, in order to ascertain whether the compounds belonging to this group of bodies behaved similarly to the Turkey-red oil acids soluble in water. The compound, which could not be obtained in the pure state, is, in many respects, similar to the Turkey-red oil acid, but the two are essentially different from each other in this respect; the sulpho-fatty acid is not decomposed by concentrated hydrochloric acid, even at a high temperature, while the acid from Turkey-red oil is easily decomposed, even by dilute hydrochloric acid, into sulphuric acid and oxystearic acid.

Turkey-red oil is, therefore, not a true sulphonic acid; it belongs, according to its whole behaviour, to the class of sulphuric ethers. The difference of constitution is made apparent by the two following formulæ for sulphated oil from olive oil:—

$$C_{17}H_{33}\left\{\begin{matrix} OH \\ SO_3H \\ CO_2H \end{matrix}\right. ; \qquad C_{17}H_{34}\left\{\begin{matrix} O\,.\,SO_3H \\ CO_2H \end{matrix}\right.$$

Oxystearic sulphonic acid. *Oxystearic sulphate.*

Ricinoleïc acid differs essentially from oleïc acid inasmuch as it contains a hydroxyl group in addition to the carboxyl group. When sulphuric acid acts on triricinoleïn (castor oil) or on ricinoleïc acid, it does not form a sulphate by addition, as is believed to be the case with trioleïn, &c., but it acts on the hydroxyl group; *a true etherification takes place with the separation of water, and a non-saturated* compound is formed—

(1) $C_{17}H_{33}CO_2H + H_2SO_4 = C_{17}H_{34}(OSO_3H)CO_2H.$

Oleïc acid. *Oxystearic sulphate.*

(2) $C_{17}H_{32}(OH)(CO_2H) + H_2SO_4 = C_{17}H_{32}(OSO_3H)CO_2H + H_2O.$

Ricinoleïc acid. *Ricinoleïc sulphate.*

The ricinoleïc sulphate may lose its sulphuric acid with or without the addition of water—

* German Patent 1,488, Sept. 30, 1877; *Dingler's Polyt. Journ.*, 254, p. 302.
† *Journ. Soc. Chem. Ind.*, 1883, p. 537.
‡ *Journ. Soc. Dyers and Col.*, 1888, p. 44.

$$(1)\ C_{17}H_{32}(OSO_3H)(CO_2H) + H_2O = C_{17}H_{32}(OH)(CO_2H) + H_2SO_4.$$

Ricinoleïc sulphate. *Ricinoleïc acid.*

$$(2)\ C_{17}H_{32}(OSO_3H)(CO_2H) + 2H_2O = C_{17}H_{33}(OH)_2(CO_2H) + H_2SO_4.$$

Ricinoleïc sulphate. *Dioxystearic acid.*

The decomposition of the ricinoleïc sulphate proceeds principally or entirely according to the first equation, and results in the formation of ricinoleïc acid, which is disposed to polymerise and oxidise. Indeed, the investigations of Juillard and of Scheurer-Kestner* indicate that Turkey-red oil (from castor oil) contains the sulphuric ethers of ricinoleïc acid and of several polyricinoleïc acids, mixed with the products of their decomposition, among which ricinoleïc acid predominates. The presence of glycerin in the commercial oil is incontestable; but it is unnecessary to make it enter into the composition of the body, as it is easily climinated without any modification of the properties of the oil.

P. Lochtin (*l.c.*) considers the ordinary Turkey-red oil to be a mixture of (insufficiently neutralised) sulpho-fatty acids and fatty acids; he ascribes but a subordinate importance to the sulpho-compounds in Turkey-red oil. He prepared an acid ammonium ricinoleate which had a composition corresponding nearly to the formula

$$(NH_4)C_{18}H_{33}O_3,C_{18}H_{34}O_3,$$

and obtained in experimental dye-trials with this so-called *acid soap*, a more even, fuller, and purer shade than in dyeing with the Turkey-red oil. The reasons why castor-oil soap (with soda), now frequently applied instead of Turkey-red oil, produces inferior results, are to be found in the fact that the solution of the soap is much more frothy than that of the neutralised sulphated oil; and chiefly, because the dyed material shows the flat and dirty shade of the alkali alizarate. This last fact is explained by the suggestion that in mordanting with alumina a waterproof envelope—ricinoleate of alumina—is formed externally on the fibre, thus enclosing the nucleus of the alkali soap. As good results as with Turkey-red oil were obtained with the soap solution by modifying in the first place the method of clearing, which was continued after boiling under pressure with weak solutions of the lime salts (gypsum, calcium chloride, calcium nitrate, &c.); in order to avoid the injurious influence of the soda as much as possible. Lochtin added sulphuric acid so as to neutralise one-half to three-quarters of the alkali present (which did not separate the fatty acid from the solution). He further prepared the above-mentioned ammoniacal oil soap and found that material oiled with this soap contains little alkali after drying, and in the alkaline clearing produces results not inferior to those obtained with Turkey-red oil.

There is some difference between the Turkey-red oil and the acid soap. The material prepared with ammoniacal Turkey-red oil shows an acid reaction after drying, the ammonium salt being decomposed and the sulpho-fatty acid producing sulphuric acid; while, on the other hand, the material oiled with the ammoniacal acid soap shows, after drying, a neutral or faintly alkaline reaction.

Scheurer-Kestner (*l.c.*) prepared a Turkey-red oil in the following manner:—One part sulphuric acid (96 per cent.) and three parts castor oil were mixed slowly, so as not to allow the temperature to rise more than a few degrees. The mixture was allowed to stand for 12 hours, and washed with 5 parts of water at 40° C. 3·7 parts Turkey-red oil were thus obtained. It was still further purified for subsequent investigation by washing with solutions of sodium sulphate.

* *Journ. Soc. Dyers and Col.*, 1891, p. 69.

The oil consists of two substances; the one (about two-thirds of the mixture) is soluble in water, and is a sulphated compound; the other (about one-third) is not sulphated. The oil never contained any unchanged castor oil.

The Turkey-red oil (the mixture of the two substances) is heavier than water and very soluble in water. If allowed to stand for several days in contact with water at the ordinary temperature it does not decompose at all; hence it is more stable than generally supposed. On boiling with twice its weight of water it becomes milky at first, but it soon separates completely into an aqueous liquid and an oil, which floats at the top. The supernatant liquid is entirely free from mineral acid; all the latter is dissolved by the water.

The non-sulphated portion is very acid, and must be either ricinoleïc acid or a polymerised derivative. It is lighter than water, insoluble in water, free from the elements of sulphuric acid, dissolves readily in caustic soda, and is precipitated without alteration by sulphuric acid. The soluble oil contains the elements of sulphuric acid in the proportion corresponding to 8·5 per cent. SO_3. It dissolves in caustic soda, and is re-precipitated by sulphuric acid without alteration. The solution of the sulphated oil in water decomposes within a few hours at 80°; but it is entirely unaffected by atmospheric conditions, and does not decompose at the ordinary temperature. It is only heat which decomposes it. The light oil is not affected by heat.

As to the brightening properties of the two substances, they are remarkable for their difference; for whilst the insoluble oil imparts to Alizarin pink a crimson, the soluble oil gives it a yellowish shade.

The composition of Turkey-red oil has also been studied with much success by P. Juillard,* and according to this author its chief constituents are: — Ricinoleïc sulphate, $C_{17}H_{32}CO_2H.O.SO_3H$, dioxystearic sulphate, $C_{17}H_{33}(OH)CO_2H.O.SO_3H$, dibasic diricinoleïc acid, $O(C_{17}H_{32}CO_2H)_2$, monobasic diricinoleic acid, $HO.C_{17}H_{32}CO_2C_{17}H_{32}CO_2H$, dioxystearic acid, $C_{18}H_{36}O_4$, an acid melting at 70° C. which probably consists of dioxystearic and ricinoleïc acid and has the formula $C_{36}H_{70}O_7$, and isoricinoleïc acid, $C_{18}H_{34}O_3$.

Turkey-red oil offers the great advantage over the ordinary soaps that it does not form curdy precipitates with the alkaline earths, but fine pulverulent precipitates which do not adhere to the textile materials in a detrimental manner.

Turkey-red oil is used in Turkey-red (Alizarin red) dyeing, in dyeing cotton with direct cotton colours and with Paranitraniline red, as a mordant for basic colours in cotton dyeing, for preparing calico before printing, in oiling wool, and in the finishing of cotton goods. Its alkaline solution acts like a soap, and is sometimes used as such.

Monopole Soap is a gelatinous substance similar in character to that of Turkey-red oil, and distinguished also by the property that its salts form, with the alkaline earths, fine pulverulent precipitates and no fatty curdy soaps like other fatty acids. It is, therefore, frequently used as an assistant with direct dyeing cotton colours and in finishing cotton goods.

Monopole Oil is a soluble oil of similar character.

TANNIN-SUBSTANCES AND ALLIED COMPOUNDS.

A number of organic acids are found in the vegetable kingdom which resemble each other in their chemical composition, and by a similar behaviour in their reactions. Their most prominent property is that of converting hide

* *Bull. Soc. Chem.*, xi., 280, 1894.

into leather. In science, however, a number of compounds which lack this latter property, almost or even entirely, are classified with the so-called tannin-substances, and it is difficult to give an exact and complete definition of this term.

In general the tannin-substances are characterised by a very astringent taste, by a feeble acid reaction towards litmus, by the property of precipitating albumen and gelatine from their aqueous solutions, and by producing either blue-black or dark green colourations with ferric salts. These properties, however, do not belong exclusively to them, but are shared with other compounds.

The tannin-substances are carboxylic acids of the aromatic series; in general, those which give blue-black colourations with ferric acetate are derivatives of pyrogallol and gallic acid, while those which afford a green colour are derived from catechol and protocatechuic acid. They are amorphous or subcrystalline solids possessing an astringent taste, are more or less soluble in water, readily soluble in alcohol and in mixtures of alcohol and ether and in ethyl acetate, but nearly insoluble in ether; in bisulphide of carbon, chloroform, petroleum spirit, and benzene they are insoluble; and, in general, they are not readily soluble in dilute sulphuric acid. Most of them can be completely extracted from their aqueous solutions by the animal skin (rasped hide or hide powder), and give precipitates with solutions of gelatine. They form precipitates with the acetates of the heavy metals, such as those of aluminium, copper, chromium, iron, lead, tin, and zinc, with tartar emetic, and with stannous and stannic salts. With the sulphates, chlorides, and nitrates no precipitates are obtained, since the tannates do not form in presence of free mineral acids. In addition they form insoluble compounds with organic bases—*e.g.*, the alkaloids of the cinchonas, and with the basic dyestuffs. The tannin-substances are powerful reducing agents; they precipitate the noble metals from their solutions in the metallic state, and possess a strong tendency, especially in alkaline solution, to absorb oxygen; the oxidation products are, as a rule, strongly coloured.

The tannin-substances are largely employed in the "tanning" of leather, in dyeing, in medicine, and for the preparation of pyrogallol, gallic acid, inks, dyestuffs, &c. Their application in dyeing is based on the fact that they are readily absorbed by the textile fibres, notably by cotton, linen, and silk; and on the property of forming insoluble compounds in the fibres, on the one hand with the heavy metals and with antimony, and on the other hand with the basic dyestuffs. In wool dyeing a special use is made of their property of precipitating certain impurities from the dye-bath so as to prevent these from being taken up by the fibre.

The following notes state briefly the character of the most important compounds connected with the tannin-substances:—

Catechol or Pyrocatechin.—*Orthodioxybenzene*, $C_6H_4(OH)_2$ [OH = 1 : 2], is formed by the dry distillation of those tannin-substances which yield green colourations with ferric acetate, and by fusing orthophenolsulphonic acid with caustic potash. It forms short white rhombic prisms, melts at 104°, boils at 245° C., and is very soluble in water, in alcohol, and in ether. It produces a green colouration with ferric acetate, which becomes violet on the addition of ammonia; and it possesses strong reducing properties. The alkaline solutions become coloured by absorbing oxygen from the air.

Guaiacol, $C_6H_4(OH)(OCH_3)$, is the methyl-ether of catechol, and is a constituent of wood-tar. Small quantities are also present in pyroligneous acid.

Protocatechuic Acid, $C_6H_3(OH)_2CO_2H$. [(OH) : (OH) : (CO_2H) = 1 : 2 : 4], is obtained by fusing catechu and other organic substances with caustic potash. It resembles catechol.

Pyrogallol or Pyrogallic Acid, $C_6H_3(OH)_3 . [OH = 1 : 2 : 3]$, is formed by dry distillation of gallic acid. It crystallises in white tablets or needles, melts at 131° C., and can be sublimated and distilled without decomposition. It is freely soluble in water, in alcohol, and in ether. It gives a blue-black colouration with ferric salts, and has very strong reducing properties; the alkaline solution rapidly absorbs oxygen from the air, being thereby coloured. It is used for the quantitative determination of oxygen in the free state, and as a developer in photography. Pyrogallol is the parent substance of those tannin-substances which are coloured blue-black by ferric salts, and of several important dyestuffs—*e.g.*, Galleïn and Coeruleïn.

Phloroglucol or Phloroglucin, $C_6H_6O_3 + 2H_2O$, is isomeric with pyrogallol, and is probably the symmetrical trioxybenzene, $C_6H_3(OH)_3$. It is obtained by fusing catechu, maclurin, quercitin, and other tannin-substances with caustic potash. Phloroglucol forms rhombic tablets, which lose their water of crystallisation at 100°, and melt at 209° to 218° C. It is readily soluble in water and in alcohol, but more so in ether; and has a very sweet taste. It does not give precipitates with metallic salts, except with basic lead acetate; with ferric chloride it gives a deep violet colouration. It is readily oxidisable, like the preceding substances.

Gallic Acid or Trioxybenzoic Acid, $C_6H_2(OH)_3(CO_2H) + H_2O . [(OH) : (OH) : (OH) : (CO_2H) = 1 : 2 : 3 : 5]$, is formed by hydrolysis of tannic acid, $C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$. It is prepared by subjecting crushed gall-nuts in water to fermentation, or by boiling tannic acid with diluted sulphuric acid. The product is obtained from the aqueous solution by evaporating and recrystallising. Gallic acid occurs as such in gall-nuts, sumach, divi-divi, and other tannin-substances, which give a blue-black colouration with ferric salts. It is probably a product of the decomposition of the tannic acid contained in them. Gallic acid forms triclinic crystals of a silky lustre, which lose their water of crystallisation above 100°, and melt with decomposition at 220° to 240° C. It is soluble in 130 parts of cold and 3 parts of boiling water, the hot saturated solution becoming a pasty mass of crystals on cooling. At 15° C. 100 parts of absolute alcohol dissolve 28 parts, diluted alcohol less, and 100 parts ether 2½ parts gallic acid. The aqueous solution has a slightly acid and astringent taste, and gradually decomposes on standing. Gallic acid is a monobasic acid, and forms crystallisable salts. The alkaline gallates are stable in the dry state; but in solution they rapidly absorb oxygen from the air, and become brown with formation of humoïd substances. Tartar emetic precipitates, even from very dilute solutions, a white precipitate of antimony gallate. On addition of ferric chloride to an aqueous solution of gallic acid an intensely blue precipitate is formed, which dissolves in an excess of the reagent with a green colour. Ferrous sulphate in the absence of air gives a white precipitate in concentrated (not in diluted) solutions; the liquid becomes bright blue on exposure to the air, and deposits a black precipitate without being decolourised. The reducing action of gallic acid is less energetic than that of the preceding compounds; Fehling's solution is only slowly and imperfectly reduced, but the salts of the noble metals are reduced by gallic acid; and an acid solution of potassium permanganate is thereby decolourised, hydrorufigallic acid, a derivative of anthracene, being formed. In contrast with tannic acid, no precipitate is formed by gallic acid in solutions of albumen, gelatine, organic bases, or starch, but a mixture of gum arabic and starch is precipitated, and in presence of sodium acetate gallic acid precipitates the basic colours from their aqueous solutions. Gallic acid has no tanning properties, and is not absorbed by cotton. On being heated slowly to 210° to 230° C. it is decomposed, and pyrogallol is formed; when heated more rapidly, and up to 250°, other products, chiefly metagallic acid, $C_6H_4O_2$, are

formed. Heated with sulphuric acid to about 140°, gallic acid is converted into rufigallic acid, $C_{14}H_8O_8$ (or hexaoxyanthraquinone). A mixture of gallic and benzoïc acid dissolved in sulphuric acid yields, on heating, anthragallol, $C_{14}H_8O_5$ (or trioxyanthraquinone, Anthracene-brown).

Gallic acid is employed in medicine, as a hair dye, in photography, and in the manufacture of certain colours (Gallocyanin, &c.).

Ellagic Acid, $C_{14}H_8O_9 + H_2O = CO\begin{cases} C_6H(OH)_3 \\ C_6(OH)_3CO_2H \end{cases} + H_2O$, occurs in myrabolans, divi-divi, pomegranate rind, and other plant products, and is formed as a bye-product in the preparation of gallic acid. Ellagitannic acid on being heated in water to 110° C. forms ellagic acid. It is also found in bezoar stones (intestinal concretions of a Persian species of goat). Ellagic acid is little soluble in water or in alcohol, and insoluble in ether; it is without taste or smell, gives with ferric chloride, at first a green and then a blue-black colouration; the alkaline solution absorbs oxygen. Ellagic acid retains with great tenacity its water of crystallisation; it forms an anhydride, $C_{14}H_6O_8$, when heated to 120° C.

Phlobaphenes are the anhydrides of the various tannic acids formed by the loss of one or more equivalents of water. They are produced by boiling the solution of tannin-substances with dilute sulphuric acid, and are always present in the barks, &c., from which the tannin materials are obtained. They are brown amorphous bodies, sparingly soluble in water, ether, alcohol, alkalies, and alkaline carbonates. Their solubility in water depends largely on their degree of hydration. The phlobaphenes are the colouring matters of the tannin-substances. They behave on the whole like the tannic acids themselves, colouring ferric salts, precipitating gelatine, and converting hide into leather. They are valuable tanning materials.

Tannic Acid or Gallo-Tannic Acid (Tannin)—*Digallic Acid.*—

$$C_{14}H_{10}O_9 + 2H_2O = \left.\begin{matrix} C_6H_2\begin{cases} OH \\ OH \\ OH \\ CO \end{cases} \\ C_6H_2\begin{cases} O \\ OH \\ OH \\ COOH \end{cases} \end{matrix}\right\} + 2H_2O.$$

It occurs in many tannin-substances, especially in nut galls, and in sumach. Nut galls contain, as a rule, 60 to 77 per cent. of it. and serve as raw materials for the manufacture of tannic acid. The galls are extracted with a mixture of water, alcohol and ether, and a solution, separated in two layers, is thus obtained; the bulk of the tannic acid is contained in the lower (aqueous) layer, and the tannic acid is prepared from this portion by evaporation. To obtain the tannin as a loose spongy mass, the syrupy solution of the same is mixed with some alcohol and ether, and then evaporated in a vacuum at a moderate temperature. The solution of tannin is caused to swell up by the escaping vapours, and is thereby formed as a loose and spongy mass, which is valued on account of its property of dissolving without difficulty. A substance resembling tannic acid has also been produced by condensation of gallic acid, and (as stated above) tannic acid has been resolved into gallic acid; hence it is supposed that it is digallic acid—$2C_7H_6O_5 - H_2O = C_{14}H_{10}O_9$.*

Tannic acid forms a colourless amorphous mass or light-yellowish to buff-coloured scales or brittle vitreous masses, and has a strongly astringent taste. It becomes yellowish in the light, even when air is excluded. On being heated,

* See, however, P. Walden, *Journ. Soc. Dyers and Col.*, 1899, p. 158.

it darkens with or without melting; and at 215° C. it decomposes, pyrogallol and metagallic acid ($C_6H_4O_2$)—a black, amorphous, tasteless mass—being the chief products; when heated rapidly to 280°, it forms metagallic acid only.

Tannic acid is soluble in 6 parts of cold water, and more freely in hot water; it is readily soluble in diluted, sparingly soluble in absolute alcohol; in absolute ether, carbon bisulphide, chloroform, petroleum spirit, and benzene it is nearly insoluble, but readily soluble in glycerin and in ethylacetate.

The aqueous solution of tannic acid gradually decomposes on standing by fermentation. Boric acid, according to P. Sisley, is the best agent to prevent this; it acts with certainty for a few days, but its action ceases if the fermentation becomes strong. Most other antiseptics are not efficient or cannot be used on account of their action on the tannin. Tannic acid is precipitated from the strong aqueous solution by diluted sulphuric or hydrochloric acid, potassium, sodium, or ammonium chloride, potassium acetate, &c.; but not by nitric acid, nor by sodium sulphate. Skin and gelatine remove it completely from the aqueous solution. Tannic acid is a weak monobasic acid; it decomposes, however, the alkaline carbonates. The salts, which are known as *tannates*, are amorphous, and it is difficult to prepare them in the pure state; most of them are insoluble in water.

Tannic acid also forms insoluble compounds with the organic bases, albuminoid substances, gelatine, &c.

SPECIFIC GRAVITY OF SOLUTIONS OF TANNIC ACID AT 15° C. (*Trammer*)

Specific Gravity.	Per Cent. Tannic Acid.	Specific Gravity.	Per Cent. Tannic Acid.	Specific Gravity.	Per Cent. Tannic Acid.	Specific Gravity.	Per Cent. Tannic Acid.
1·0040	1·0	1·0084	2·1	1·0124	3·1	1·0164	4·1
1·0044	1·1	1·0088	2·2	1·0128	3·2	1·0168	4·2
1·0048	1·2	1·0092	2·3	1·0132	3·3	1·0172	4·3
1·0052	1·3	1·0096	2·4	1·0136	3·4	1·0176	4·4
1·0056	1·4	1·0100	2·5	1·0140	3·5	1·0180	4·5
1·0060	1·5	1·0104	2·6	1·0144	3·6	1·0184	4·6
1·0064	1·6	1·0108	2·7	1·0148	3·7	1·0188	4·7
1·0068	1·7	1·0112	2·8	1·0152	3·8	1·0192	4·8
1·0072	1·8	1·0116	2·9	1·0156	3·9	1·0196	4·9
1·0076	1·9	1·0120	3·0	1·0160	4·0	1·0200	5·0
1·0080	2·0						

Tannic acid is readily oxidisable, and reduces the salts of the noble metals, of mercury and of copper, the permanganates, &c. The alkaline solution of tannic acid rapidly absorbs oxygen from the air, and acquires a brown colour by decomposition. If air is passed through a solution of tannic acid for a certain length of time, a yellow colouring matter—galloflavin—is produced. Ferrous sulphate gives in concentrated aqueous solutions a white precipitate which turns blue on access of the air. Ferric salts produce a bluish-black precipitate of ferric tannate or "ink"; the colour is destroyed by boiling or by reducing agents; the precipitate dissolves in hydrochloric acid, and is thrown down again by sodium acetate. An ammoniacal solution of cupric sulphate is precipitated by tannic acid; and Fehling's solution is reduced on heating, yellow or red cuprous oxide being formed. From a solution of cupric acetate, tannic acid precipitates green tannate of copper. With the soluble salts of antimony, bismuth, lead, tin, zinc, &c., white precipitates are formed which are soluble in acids. Tannic acid forms no precipitate with calcium acetate in the

presence of acetic acid, and the solution remains clear on adding alcohol; by this reaction it can be separated from oxalic, tartaric, citric, and similar organic acids.

Tannic acid forms a white or buff-coloured flocculent precipitate with a solution of gelatine which is entirely insoluble in an excess of tannic acid, but not wholly insoluble in pure water; when freshly formed it is often extremely finely divided; but it is rapidly coagulated by ammonium chloride, alum, and other salts. This precipitate is considered to be the basis of leather; but tannic acid itself is not a suitable material for tanning hides and producing leather. As stated before, tannic acid, on being heated above 200°, forms pyrogallol and metagallic acid; on being heated with dry arsenic acid it produces ellagic acid ($C_{14}H_8O_9$); and a solution of tannic acid forms on boiling with ammonium sulphate gallaminic acid.

Tannic acid is used in pharmacy, in dyeing, and in printing, in the preparation of inks and dyestuffs, pyrogallol, gallic acid, &c.

Ellagitannic Acid, $C_{14}H_{10}O_{10}$, is contained in divi-divi, myrabolans, and as a glycoside in the rind of the pomegranate. It is a brown amorphous mass which is converted into its anhydride, ellagic acid, on being heated with water to 110° C. It yields a light brown precipitate with cupric acetate; and with lead acetate in alcoholic solution a white precipitate of ellagitannate of lead. In general it strongly resembles tannic acid.

Quercitannic Acid, $C_{19}H_{16}O_{17}$ (?), is the tannin of oak-bark where it occurs, together with its own anhydride or phlobaphene, with gallic acid, ellagic acid, and various kinds of sugar. It can be prepared from oak-bark by successive extraction with alcohol, ether, and ethyl acetate, and forms a reddish-white amorphous powder, soluble in water, alcohol, and ethyl acetate, but not in ether or benzene.

Quercitannic acid gives a blue-black colour and, after some time, a precipitate with ferric chloride; it yields yellowish-white precipitates with albumen, gelatine, organic bases, and antimony salts; precipitates are also formed with lead acetate and ammoniacal solutions of zinc or magnesium chloride and of copper sulphate or acetate. The exact composition of quercitannic acid is not known; it is probably a derivative of gallic acid. Quercitannic acid loses water when heated to 130° to 140° C., and when boiled with very dilute sulphuric acid, as also with caustic alkalies or alkaline carbonates; and forms several anhydrides known as *phlobaphene*, *oak-bark red*, &c., which are brownish-red substances, sparingly soluble in water, but soluble in solutions of quercitannic acid. Their composition is very uncertain; they show the characteristic reactions of tannin-substances, and possess tanning properties. They are not employed in dyeing. Quercitannic acid and its anhydrides (in the form of oak-bark) are the most important materials for the tanning of leather.

Catechutannic Acid and Mimotannic Acid are probably identical substances. They are obtained from catechu and from gambier, but their composition is uncertain. They resemble tannic acid, but differ from it in the following reactions:—They yield greyish-green precipitates with ferric salts and no reactions with ferrous salts; with cupric sulphate they give a dense precipitate, but none with antimony salts. The composition of catechutannic acid has been stated to be $C_{21}H_{18}O_8$; it is a dark reddish-brown powder, soluble in water, alcohol, and ethyl acetate, but not in ether. The aqueous solution is precipitated by sulphuric acid, by albumen and gelatine.

Catechin, $C_{15}H_{14}O_6$, crystallises in small needles having the composition $C_{15}H_{14}O_6 + 3H_2O$ or $C_{15}H_{14}O_6 + 4H_2O$. It is readily soluble in hot water, in alcohol, and in ethyl acetate, and moderately soluble in ether. It gives a green colouration with ferric chloride, has reducing properties, but does not

give precipitates with organic bases or gelatine or antimony salts. Catechin occurs in catechu and in gambier; catechutannic acid is the first anhydride of catechin; other anhydrides are also known. The constitution of all these substances is uncertain. Catechin yields by decomposition catechol, protocatechuic acid and phloroglucol. When exposed to the air it is converted into a brown insoluble substance, known as *japonic acid.*

Description of the Tannins used in Dyeing.—A number of tannin-substances are employed as mordants in the dyeing of the textile fibres. Some of these substances are used on account of their lower prices as substitutes for tannic acid in mordanting; hence they are here classified with this body as tannins. A number of tannin-substances, however (notably catechu), are not used as mordants, but as real colouring matters, hence they will not be included in the term "tannin" as here understood. Among the tannins myrabolans and sumach are next in importance to tannic acid, then follow valonia, divi-divi, knoppern, chestnut extract, quebracho, and others. Instead of pure tannic acid the extract of gall-nuts is also used. Tannic acid is most generally employed in mordanting cotton for bright shades, and for medium and dark shades myrabolans, sumach, and sumach extracts find very large application on this fibre; the other tannins are chiefly used for the weighting of black silk.

Galls are the excrescences on plants, produced by the punctures of certain insects for the purpose of depositing their eggs.

(1) **Oak-Galls** are produced by the female gall-wasp (*Cynips gallæ tinctoriæ*, Oliv.), which drops an egg in the rind of young branches of certain oaks. A swelling (the gall-nut) is formed in which the young insect develops, and from which it finally escapes by piercing a hole through the shell. Those galls which are not pierced contain most tannic acid; they have a fresh green or blue colour, and are heavy—*green or blue galls.* If the insect has escaped, they are yellow and lighter, and of inferior quality—*white galls.*

The best oak-galls are the *Aleppo galls*, which come from Persia or the East Indies *viâ* Aleppo, and the *Turkish* or *Levant galls* (Tripoli, Smyrna, Corea, &c., galls); they contain 55 to 60 per cent. tannic acid, and about 4 per cent. gallic acid. The Italian, Hungarian, French, and German galls are of greatly inferior quality.

The holes of worm-eaten galls are sometimes filled up with wax; by immersing them in boiling water the wax will melt and the holes become visible. Extracted galls have been covered with a solution of ferrous sulphate, which is readily detected by the usual reactions for iron.

(2) **Chinese and Japanese Galls** are produced by the puncture of a plant-louse (*Aphis chinensis*, Doubl.) on the leaves and leaf-stalks of *Rhus semialata.* They are very light and hollow, and very rich in tannic acid (65 to 70, and even as much as 77 per cent.). The Japanese galls are smaller than the Chinese, and are more valued. Both are used chiefly for the production of tannic acid.

Knoppern are galls formed by the puncture of a gall-wasp in the immature fruit of a species of oak growing in Austria. They contain from 25 to 35 per cent. tannic acid, and are largely employed in tanning, but are less suitable for dyeing than the other galls.

Tannic Acid, $C_{14}H_{10}O_9$ (see p. 181).

Sumach consists of the leaves and twigs of several species of Rhus; the sumach from *Rhus coriaria* is the best, and Sicilian sumach is the finest commercial quality. Next come the Spanish, Portuguese, Greek, and Virginian (U.S.A.) sumachs; inferior qualities are the sumachs from Provence, Hungary, and the Tyrol, which are derived from *Coriaria myrtifolia* and *Rhus cotinus*, and cannot replace the sumach from *Rhus coriaria.* Sumach is sold in the form

of the whole or crushed leaves, or as a powder; the leaf-stalks and small twigs are often admixed. Best sumach contains 15 to 20 per cent. tannin, and has an olive-green colour and a fresh agreeable smell. The sumach, which is dull in colour and smell, has been deteriorated by moisture and long keeping. Sumach contains some reddish colouring matter, which prohibits it from being employed for the dyeing of light and brilliant shades; the Sicilian sumach is the least coloured; it contains gallotannic acid.

Sumach Extract is manufactured in large quantities as a thick dark-brown liquid of about 52° Tw. Excellent qualities of decolourised sumach extract are now offered, which can replace tannic acid even for light shades.

Myrabolan is the fruit of several kinds of trees growing in China and the East Indies (*Terminalia chebula*, Willd.; *Myrabolanus chebula*, Gaert.). The dried fruits resemble a slightly shrivelled plum, are about an inch long, very hard, and possess a bitter astringent taste. The stones contain little tannin; the bulk is in the peel (25 to 45 per cent. in the whole fruit). The tannin of the myrabolan is ellagitannic acid. Myrabolan contains a yellowish-brown colouring matter, which, when removed, makes this material a good substitute for tannic acid in many applications. It is used in tanning, in cotton dyeing, and in the black dyeing of silk.

Divi-Divi or **Libi-Divi** is the leguminous fruit of a small tree (*Cæsalpinia coriaria*, Willd.) found in the West Indies and South America. The pods are about 3 inches long, ½ to ¾ inch broad, and very thin; they are often folded up in the shape of a letter **S**. They have a lustrous brown or blackish colour externally, and a yellowish one internally; the lightest coloured are the best. The tannin-substance is ellagitannic acid (19 to 35 per cent.); they also contain gallic acid. Divi-divi is used for tanning and black dyeing.

Valonia consists of the acorn cups of certain species of oak from Asia Minor, Greece, the Grecian Archipelago, and the South of France (*Quercus ægilops*, *Quercus græca*, and *Quercus vallonea*). They have a diameter up to 1½ inches, and should possess a bright drab colour. Their tannin-substance is tannic acid (25 to 35 per cent. and sometimes more) accompanied by a dirty-yellow colouring matter.

Bablah or **Nebheb** is the leguminous fruit of several species of Acacia (*Acacia Arabica*—East Indian bablah, and *Acacia nilotica*—Egyptian bablah). The fruits contain nearly 20 per cent. tannin-substance. The extract has a sweetish, little astringent taste. Bablahs are used for tanning and for black dyeing.

Chestnut.—The extract is prepared from the wood of the chestnut-oak (*Æsculus hippocastanum*). The composition of the tannin-substance is not known; it yields a green colouration with ferric chloride, precipitates gelatine solutions, and produces, when fused with caustic potash, protocatechuic acid and phloroglucin.

The wood contains 8 to 10 per cent. tannin. The solid extract has a brilliant black colour; the liquid extracts are brown syrups, possess an astringent taste, and smell like burnt sugar. On diluting with water they become turbid and yield brown phlobaphenes, which apparently take part in the dyeing process. Chestnut extract is the most important tannin for the black dyeing of silk.

In the foregoing are named the principal tannin-substances used in mordanting and black-silk dyeing. A number of other similar bodies (catechu, gambier, and fustic) will be described amongst the dyestuffs.

THE APPLICATION OF THE TANNIN-SUBSTANCES OR "TANNINS" TO THE TEXTILE FIBRES.

Application to Cotton and Linen.—Cotton and linen evince little power to attract and retain most dyestuffs so as to yield full and fast shades. They possess, however, the property of taking up and fixing considerable amounts of certain substances which are able to form insoluble compounds with dyestuffs. It cannot be decided whether the fibres exert a chemical action towards these substances; for, as yet, no proof of any affinity has been found.

Cotton and linen possess a remarkable power of attracting tannins from their aqueous solutions; the quantity which is taken up by the fibre from the liquor depends chiefly on the concentration of the latter and on the quantity of other substances, like sulphuric acid, common or Glauber's salt, &c., which may be present. According to Juste Koechlin, cotton, which has been saturated with a solution containing 50 grms. tannic acid per litre, still continues to absorb more tannin when steeped in a solution containing 20 grms. per litre only. It retains the whole of its tannic acid in a solution of 5 grms. per litre, and only begins to lose it in a solution of 2 grms. per litre. Acids and salts precipitate the tannin from its aqueous solutions, and, if added to the latter, cause them to be better exhausted.

The actual amounts of tannic acid taken up by cotton under various conditions have been determined by Knecht & Kershaw.*

In the experiments, except where otherwise stated, were used 5 grms. of cotton, 5 per cent. of tannic acid, and 30 times the weight of water (of the weight of the cotton). The cotton was entered at 100°, and was allowed to cool with occasional stirring during three hours.

The following is a résumé of the results obtained:—

EFFECT OF TEMPERATURE.

1. The cotton was steeped cold for three hours.
2. The cotton was entered boiling and allowed to cool during three hours.
3. The cotton was steeped at 50° for three hours.
4. The cotton was steeped boiling for one hour.

RESULTS.

	Tannic Acid Taken.	Absorbed by Cotton.	Left in Solution.
	Grm.	Grm.	Grm.
1	0·25	0·0363	0·2137
2	0·25	0·0513	0·1987
3	0·25	0·0082	0·2418
4	0·25	0·0025	0·2475

EFFECT OF CONCENTRATION.

The cotton was entered boiling and allowed to cool during three hours, but with varying amounts of water, viz.:—

1. 75 c.c. water. 2. 150 c.c. water. 3. 300 c.c. water. 4. 450 c.c. water.

RESULTS.

	Tannic Acid Taken.	Absorbed by Cotton.	Left in Solution.
	Grm.	Grm.	Grm.
1	0·25	0·0663	0·1837
2	0·25	0·0513	0·1987
3	0·25	0·0288	0·2212
4	0·25	0·0238	0·2262

* *Journ. Soc. Dyers and Col.*, 1892, p. 40.

EFFECT OF TIME.

The cotton was entered boiling and allowed to cool as above. The original conditions were again adhered to, but the time was altered.

RESULTS.

Tannic Acid Taken.	Absorbed by Cotton.	Left in Solution.	Time.
Grm.	Grm.	Grm.	
0·25	0·0128	0·2372	30 min.
0·25	0·0168	0·2332	1 hr.
0·25	0·0490	0·2010	2 hrs.
0·25	0·0572	0·1928	4 hrs.
0·25	0·0609	0·1891	6 hrs.

The tannin is still being absorbed after six hours' immersion, and although the absorption is not in a direct ratio to the time of immersion, the limit has not been reached in six hours.

CONSECUTIVE BATHS.

1. 5 grms. cotton were entered boiling and allowed to cool during 1½ hours.
2. Same as No. 1. Wring out well, then enter a second 5 grms. at 100° and allow to cool again during 1½ hours.
3. Same as No. 2, with a third lot of cotton.

RESULTS.

Tannin Used.	Absorbed by 1st 5 Grms.	Absorbed by 2nd 5 Grms.	Absorbed by 3rd 5 Grms.	Left in Solution.
Grm.	Grm.	Grm.	Grm.	Grm.
0·25	0·0355	...	...	0·2145
0·25	0·0355	0·0195	...	0·1950
0·25	0·0355	0·0195	0·0103	0·1847

EFFECT OF WASHING OUT.

Enter boiling and allow to cool overnight.

Absorbed by Cotton.	Left in Solution.
Grm.	Grm.
0·0612	0·1888

1. Steep in cold water (150 c.c.) for one hour.
2. Steep in cold water (150 c.c.) for three hours.
3. Steep in boiling water for one hour.
4. Enter into a solution of 10 per cent. tannic acid (of the weight of the cotton) at boil and allow to cool during three hours.
5. As No. 4, using 2½ per cent. tannic acid.

RESULTS.

	Left in Fibre.	Tannin Extracted.
	Grm.	Grm.
1	0·0465 } out of 0·0612	0·0147
2	0·0393 } out of 0·0612	0·0221
3	None } out of 0·0612	0·0612
4	0·0198 + the 0·0612 absorbed	...
5	0·0007 lost	...

BLEACHED, UNBLEACHED, AND MERCERISED COTTON.

The cotton was entered boiling and allowed to cool during three hours.

Material.	Tannic Acid Taken.	Absorbed.	Left in Solution.
	Grm.	Grm.	Grm.
Bleached Cotton, . .	0·25	0·0513	0·1987
Unbleached ,, . .	0·25	0·0568	0·1932
Mercerised ,, . .	0·25	0·1033	0·1467

The unbleached cotton was boiled previously for a short time with soap, to remove waxy and other impurities.

Precipitated Cellulose is capable of absorbing under similar conditions a much larger proportion of tannin than cotton yarn. By using 5 grms. of such cellulose. 150 c.c. water, entering at 100° C., and allowing to cool during three hours, the following results were obtained:—

Tannic Acid Taken.	Absorbed.	Left in Solution.
Grm.	Grm.	Grm.
0·25	0·1525	0 0975

According to G. v. Georgievics * the process of the absorption of tannin by the cotton fibre may be expressed by the formula

$$\frac{\sqrt{C \text{ bath}}}{C \text{ fibre}},$$

the term C fibre denoting the amount of tannin absorbed by the cotton, whilst C bath refers to the amount of tannin remaining in the water after the operation.

Gardner and Carter † found that the cotton absorbs larger quantities of tannin and also some gallic acid, if the bath contains some acetic acid; 5 grms. acetic acid were found to be the most suitable amount for solutions of 1 grm. tannic acid in 1 litre of distilled water. Formic and propionic acid act in the same way, but not so citric or tartaric acid. Sulphuric acid has an action opposite to that of acetic acid (see Knecht and Kershaw). Hydrochloric acid has almost no effect at all.

The tannins play an important part in cotton dyeing, and are largely used for preparing cotton, so as to enable it to retain colouring matters permanently. Cotton when impregnated with a solution of Magenta acquires a more or less intense bluish-red tint; the colour, however, can be easily removed by water. If the cotton had been previously impregnated with tannic acid, it attracts the dyestuff much more rapidly, and it is, under certain conditions, impossible to strip the colour by water. Frequently the purpose of preparing the vegetable fibres with tannin is not so much to fix the colouring matters themselves, although that is the ultimate aim, as to fix certain metallic oxides (notably the oxides of aluminium, copper, tin, and iron), in the form of insoluble tannates, which oxides fix the dyestuffs in the fibre by forming insoluble lakes with them during the subsequent dyeing process.

Tannic acid is the best "tannin" for the mordanting of cotton and linen, since it is the purest of all, and does not contain the natural impurities of the other materials, which are partly ineffective, partly injurious in mordanting and dyeing. It is especially more free from colouring matter than any other

* *Journ. Soc. Dyers and Col.*, 1898, p. 234. † *Ibid.*, p. 143.

tannin. Tannic acid is almost exclusively used in the dyeing of light and brilliant shades, so that all the instructions given later will refer to pure commercial tannic acid. For dark shades extracts of gall-nuts, sumach, and myrabolans are largely employed, but the other materials find little application in cotton dyeing. Gall-nuts and decolourised sumach extracts give the best results next to tannic acid, the quantity used depending on the amount of tannic acid they contain—as a rule, about five to ten times as much as pure tannic acid is required. Cotton is prepared with tannin in the loose state, in the yarn, and in the piece, after the material has passed through the required cleansing and, if necessary, bleaching operations. Loose cotton and cotton yarn are soaked for some time in more or less diluted solutions, whereas cotton pieces can also be impregnated with strong solutions by the padding method.

Steeping Method.—A bath is prepared with 2 to 5 per cent. tannic acid (of the weight of the material), and a sufficient quantity of water to work the material (20 to 30 times the weight of the material). For very dark shades 5 to 10 per cent. tannic acid is required. The bath is used hot or cold. Cotton does not extract much tannin from the solutions above 60° C.; yet hot solutions are employed to saturate the material quicker with the liquor, and to drive out all the air from the fibre. The cotton is worked in this liquor for some time, and soaked for from three to twelve hours—overnight—while the bath cools. Mixed goods are not mordanted at a high temperature (see below). The material being sufficiently saturated, the excess of liquor is removed mechanically, and a light washing with water follows.

Padding Method.—Cotton piece goods are mordanted with tannin in the padding machine or jigger, because this process works more rapidly. For dyeing with basic colours, the pieces are run through a warm solution of tannic acid (2° to 3° Tw.), pressed out between squeezing rollers, beamed, and left for one to two hours. For blacks and for some basic colours, like the dark blues, stronger tannin liquor is taken.

Mixed cotton goods, containing either wool or silk, are mordanted at the ordinary temperature, so that the cotton only may take up tannin, and not the wool or silk.

The tannin-baths can be used continuously. They are exhausted more completely by additions of common salt or other salts, or acetic acid, which diminish the solubility of the tannic acid in water. Steel and Grandage recommend the addition of 10 to 15 per cent. (of the weight of the tannin) common salt, 2 per cent. salammoniac, and 1½ per cent. borax.

Cotton and linen retain the absorbed tannin, even resisting a moderate washing; but by continued washing and soaping the tannin is stripped.

Tannic acid forms lakes with the basic colours, which are insoluble in pure water, but dissolve in an excess of tannin and in other acids. The tannic acids can be converted into various metallic salts, which are insoluble in tannic acid or in water, and which, when produced in the fibre, resist soaping very well. These insoluble salts possess the same property as tannic acid in the free state of forming lakes with the basic colours; but an excess of the salts has no dissolving action on the colour-lakes, and the products are very stable. There are in this way produced in the fibre *triple compounds* of tannic acid, a metallic oxide, and a basic colour, which are quite insoluble in water, and resist both washing and soaping extremely well; and they are also faster to light than the lakes of tannin and colouring matter which do not contain a metallic oxide.

Antimony holds the first place as a fixing agent of tannin in dyeing with the basic colours; it yields the fastest colours both in regard to soap and to light; very good results are obtained with tin, less good with zinc; aluminium

salts are used in special cases, and those of iron are only employed for the production of dark shades. The dark colour of the iron tannate does not permit its application for light shades, but effects a saving of dyestuffs in dark colours; in such a case the tannate of iron plays the double part of mordant and ground colour. The exact methods of fixation will be given in the chapters on the dyestuffs and metallic mordants.

In the inverse case of tannin being the fixing agent for a metallic oxide, the latter being the mordant proper, the material is impregnated in exactly the same way with tannin as described above.

Application to Wool.—Wool has so slight an affinity for tannin that the tannins are seldom applied to this fibre. Solutions of tannins have a tendency to render the wool fibre harsh or "hask," especially if used at high temperatures, and great care must be taken to avoid this fault in the dyeing of mixed fibres. Tannic acid prevents, to a certain extent, the fixation of other colouring matters on wool. It is noteworthy that chromed wool which has been boiled or steeped in solutions of tannin cannot be dyed black with logwood. The colours thus obtained are browns, which are not fast to light. Tannic acid is sometimes added to the dye-bath in dyeing Alizarin colours on wool to prevent them from rubbing.

Application to Silk.—The tannins are extensively employed in the preparation of silk, both to strengthen and to weight the fibre. It seems that the tannins act in a similar manner on the silk fibre as on the animal skin, in so far as both lose their endosmotic and exosmotic properties on being saturated with these bodies. Silk loses, on being mordanted with tannins, in a remarkable degree the property of absorbing ferric salts (not ferrous salts) or dyestuffs, but it regains this power if the tannin is transformed into an insoluble tannate.

For the production of light shades the silk is worked and soaked in a cold solution of tannic acid or an extract of gall-nuts prepared without heating; it takes up in this way from 12 to 15 per cent. of its own weight. The impregnation takes place after the dyeing, since the tannin would be decomposed to some extent by the hot soap employed in dyeing, and the shade would be dulled. The colouring matter of tannin has, in any case, a deteriorating influence on light tints.

As full and dark shades are less sensitive, they allow of mordanting being effected at elevated temperatures and with inferior (*i.e.*, more strongly coloured) tannins, especially sumach and myrabolans; for black the divi-divi or cheaper chestnut extracts are largely employed. The preparation with tannin takes place at about 70° C., and the weight of the silk is thus increased by about 25 per cent. The greatest absorption takes place at incipient boiling, but the increase is not considerable above 70° C.

In order to achieve a heavy weighting with tannin, the silk is treated alternately with tannin and with glue in the form of gelatin previously heated with nitric acid, the tannin and the glue forming an insoluble compound in the fibre, and thus yielding a weighting of more than 100 per cent. on souple silk.

The silk, which has been completely saturated with tannin, can be made to take up fresh quantities of the same by a treatment with ferrous salts. The material is worked in a strong solution of pyrolignite of iron, and exposed to the air to oxidise the ferrous tannate thus formed. It is then able to absorb fresh quantities of tannin. Use is made of this method in black dyeing.

Silk which contains tannin in the free state cannot be treated with a ferric salt, because it has lost its endosmotic property, and the ferric salt would simply destroy the tannin by oxidation. The case is different if the silk is first impregnated with a ferric salt and then passed through tannin liquor; in

this manner ferric tannate is formed and the endosmotic property preserved; the silk is thereby enabled to take up alternately fresh quantities of ferric salt and tannin. The operation is best executed at 40° to 50° C.; at higher temperatures, especially above 70° C., ferric oxide exerts too great an oxidising action on tannin. Silk is "weighted" by this method in black dyeing up to 200 per cent. of its own weight.

In the description of the iron mordants, particulars are given as to the treatment of silk with ferrous and ferric salts.

Tannin is also applied to silk which has been dyed with Prussian blue for weighting purposes. In this case, however, catechu and gambier are generally used. Frequently tin crystals are added to the tannin to increase the weight of the silk.

Silk dyed with Prussian blue takes up large quantities of tannin, which may vary, however, according to the temperature. Below 50° C. the silk absorbs 10 to 12 per cent. tannin without the Prussian blue itself being affected. At a temperature between 50° and 70° C. the Prussian blue is partially reduced, according to Moyret, by a portion of the tannin; and the oxides thus formed combine again with tannin, producing an increase of 30 to 40 per cent. and even more of the weight of the silk. By the treatment with tannin, the blue silk is rendered capable of resisting hot soaping without the Prussian blue being decomposed. The addition of stannous chloride is used for heavy weighting only; for an increase of the weight of more than 20 to 30 per cent. after the blueing, 5 to 15 per cent. tin crystals are added to the tannin-baths, which are heated to 70° or 75° C.; the temperature must not be higher. The hanks of silk must be worked very close together in the tin-tannin-baths, so as to exclude the air as much as possible; for the same reason, the vat should be well filled with liquor. The oxidising influence of the air causes the material in the bath to assume a cloudy yellowish appearance, but, on washing with water, the full colour is restored.

The working in the tannin-bath lasts at least one hour; the goods may also be left overnight in the bath without being injured. The tannin-baths are used continuously; the tin-tannin-baths are allowed to settle, and the clear liquor is used afresh; the tin which is contained in the sediment may be recovered by the process described for tin.

The tanned silk is finally rinsed in water and soaped in boiling hot solution of oil soap (30 to 40 per cent. of the weight of the silk) for two hours; for the soaping, an old logwood bath is used with advantage. The silk may then be brought back to the tannin-bath, or finished in alkaline and acid olive oil (softening and brightening).

Silk which has been dyed with direct colours, either acid or basic dyestuffs, is frequently treated with tannins and metallic salts, in order to make the colours faster so as not to run in water. For light shades, best tannic acid is used in combination with a salt of antimony, whilst, for dark shades, most frequently cutch or gambier and stannous chloride are employed. The dyed silk is turned a few times in a fairly strong bath of tannin at 30° to 40° C., and steeped therein overnight; the next day it is rinsed, passed through a lukewarm solution of an antimony salt (5 to 15 grms. per litre), or through a solution of stannous chloride (30 to 35 grms. per litre) in dilute acetic acid, rinsed and softened, if necessary, or brightened. The colours thereby become much faster to water and also fairly fast to washing.

According to Leo Vignon,* boiled-off silk absorbs about 25 per cent. tannic acid (calculated on the weight of the silk), but very little gallic acid.

* *Comptes rendus* (1895), cxxi., p. 916.

BASES AND SALTS.

Potassium Hydroxide or Caustic Potash, KOH—*Potassium Hydrate.*—Potassium hydrate is a white crystalline mass which melts below red heat, and is volatile at higher temperatures. It dissolves in half its weight of water and is very hygroscopic and deliquescent; the solution is called caustic potash-lye. Caustic potash is also very soluble in alcohol.

Potassium hydroxide is the strongest of all bases and is monacid; it possesses strong caustic properties and a caustic taste, and attracts carbon dioxide from the air to form potassium carbonate. Potassium hydroxide is manufactured by decomposing potassium carbonate with lime. It is used in the arts and in the laboratory. Sodium hydroxide, however, which strongly resembles it, is used in most cases, being considerably cheaper.

Potassium Carbonate, K_2CO_3—*Carbonate of Potash; Potash.*—Potassium carbonate is the chief constituent of the ashes of land plants. In former times it was obtained exclusively by extracting these ashes with water; great quantities are now manufactured on the large scale from potassium chloride (mined in Stassfurt) by the Leblanc process (see *Sodium Carbonate*).

Potassium carbonate is a white substance which absorbs moisture from the air and is deliquescent; it crystallises with $1\frac{1}{2}$ molecules of water of crystallisation, $K_2CO_3 + 1\frac{1}{2}H_2O$. The solution has a caustic taste and shows alkaline reaction. It combines with carbonic acid, forming *potassium bicarbonate* ($KHCO_3$), which dissolves in three to four parts of cold water, is not deliquescent, and has a neutral reaction. Potassium carbonate is used in various industries, especially in the manufacture of soft soaps and of fine glass ware. It is used to a small extent only by dyers. In most cases sodium carbonate, which is very similar, is used, as it is much cheaper than the potassium salt.

Potassium Percarbonate, $K_2C_2O_6$—*Percarbonate of Potash.*—This salt (and, analogously, the sodium and ammonium salts) is obtained by the electrolysis of saturated potash solutions, cooled to 10° to 16° C. Its aqueous solution readily decomposes with formation of potash, carbon dioxide, and oxygen, which has a strong oxidising and bleaching effect; with acids it forms carbon dioxide, oxygen, and hydrogen peroxide, and, with caustic lyes, oxygen only. It is a powerful bleaching agent, and, if produced at a low price, it might supplant sodium or hydrogen peroxide, &c.

Potassium Hypochlorite, $KClO$—*Eau de Javelle; Chloride of Potash.*—Potassium hypochlorite is known only in aqueous solution, which is obtained by the action of chlorine gas on caustic potash solution, or by double decomposition of chloride of lime and potassium carbonate, and is known under the name of *Eau de Javelle.* It is a strong bleaching agent, and was formerly used in the household for bleaching purposes, but has been entirely displaced by the cheaper bleaching powder and by the solution of sodium hypochlorite, which is also frequently called "Eau de Javelle."

Potassium Chlorate, $KClO_3$—*Chlorate of Potash.*—Potassium chlorate is obtained by saturating caustic potash solution with chlorine gas; on the large scale, a mixture of lime and potassium chloride is used—$3Cl_2 + 6KOH = KClO_3 + 5KCl + 3H_2O$. Potassium chlorate crystallises in shining tables belonging to the monoclinic system. The crystals are not very soluble in cold water, 100 parts water dissolving 6 parts of the salt at 15° C., and 60 parts at the boiling temperature. On being heated above its melting point (359°) potassium chlorate gives off oxygen. Chlorate of potash is a powerful and convenient oxidising agent. In dyeing and printing, it is employed in the production of Aniline black and some other colours (for instance, manganese bronze), as also for the preparation of mordants.

Potassium Chromate and **Bichromate** (see *Chromium*).

Potassium Sulphocyanide or **Thiocyanate**, KCNS, crystallises in transparent prisms, which are deliquescent and melt readily on heating. It is very soluble in water, and absorbs a great quantity of heat on dissolving. It is used as a reagent for ferric salts, and may be employed to neutralise acids which are liable to carry iron into the colours.

Potassium Ferrocyanide, $K_4Fe(CN)_6 + 3H_2O$ — *Yellow Prussiate of Potash.*—This salt is prepared by heating iron and potash with nitrogenous substances (animal refuse, such as clippings of horn, hoof, leather, &c.). It forms lemon-yellow crystals, containing water of crystallisation. It has a sweet-bitter saline taste and is not poisonous. It dissolves in 4 parts of cold and 2 parts of hot water, and is insoluble in alcohol. The solution on being boiled becomes alkaline, evolving ammonia and hydrocyanic acid (see *Prussian blue*). Potassium ferrocyanide is used for the production of Prussian blue and in Aniline-black dyeing. It forms precipitates with the basic aniline dyestuffs, and may be employed as a mordant for these on cotton.

Potassium Ferricyanide, $K_3Fe(CN)_6$—*Red Prussiate of Potash.*—This salt is manufactured by treating the yellow prussiate with oxidising agents like chlorine. It crystallises in dark-red prisms which contain no water of crystallisation. 100 parts of cold water dissolve about 35 parts, hot water twice as much of the salt. Potassium ferricyanide acts as an oxidising agent, especially in presence of caustic soda. It is used as a discharge in printing and in the production of Prussian blue.

Potassium Oxalate, $K_2C_2O_4 + H_2O$.—Forms rhombic crystals, which are soluble in 3 part of cold water.

Acid Potassium Oxalate, $KHC_2O_4 + H_2O$—*Binoxalate of Potash.*—It forms monoclinic crystals, soluble in about 25 parts cold water.

Binacid Potassium Oxalate, KHC_2O_4, $H_2C_2O_4 + 2H_2O$.—Triclinic crystals, which are soluble in about 50 parts of cold water.

Commercial binoxalate of potash, or *salt of sorrel*, commonly known as "salts of lemon," is a mixture of the two acid oxalates. It is sometimes used as a mild acidifying substance, also as a substitute for tartar.

Acid Potassium Tartrate, $C_4H_4O_4(OH)(OK)$—*Cream of Tartar, Tartar, Argol.*—This salt is obtained from the deposit which forms on the bottom of the vessels in which the fermentation of wine proceeds. In the crude state it is called "argol"—red or white, according as it is obtained from red or white wine; the ordinary purified product is known as "tartar," while "cream of tartar" is nearly pure acid potassium tartrate. The pure salt forms rhombic crystals; the commercial product is sold as a powder.

Solubility of acid potassium tartrate, in 100 parts of water, at—

10° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
Part. 0·40	Part. 0·57	Part. 0·90	Parts. 1·3	Parts. 1·8	Parts. 2·4	Parts. 3·2	Parts. 4·5	Parts. 5·7	Parts. 6·9

Tartar is used in considerable quantities as an assistant in the mordanting of wool with salts of aluminium, chromium, iron, copper, and tin, and serves to improve the permanence, fulness, and brilliancy of the ultimate colour. This influence is probably due to a double decomposition of the tartrate and the mordanting salt, the mineral acid of the latter combining with the potassium of the tartrate and the metallic hydrate with tartaric acid; it is also possible that a double salt is formed. At all events, it seems that the mordanting salt is changed in such a way that the fibre takes it up more

readily and a better result is obtained. By mordanting wool with pure tartrates of aluminium, &c. (see *Aluminium on Wool*), excellent results are obtained. If, moreover, the tartaric acid which has been absorbed by the fibre is not properly washed out, it will, no doubt, exert a less injurious effect in dyeing than sulphuric acid in the free state (*Hummel*). Sometimes, as, for instance, in mordanting with bichromate and tartar, the latter salt acts also as a reducing agent.

A number of preparations have become known under the name of *substitute of tartar*, *superargol*, &c. Some are simply acid sodium sulphate; others contain oxalates; while still others are tartar, which contains sufficient sulphuric acid to convert all the potassium into potassium sulphate. In so far as these preparations claim to replace tartar completely, most of them are a direct fraud, because they cannot produce the double decomposition between the mordanting salt and a tartrate; if it is intended to use them for acidifying only, well-known and analysed chemicals—such as tartaric or oxalic acid or sodium bisulphate—should be preferred to preparations of unknown composition and properties.

Sodium Hydroxide or **Caustic Soda**, NaOH—*Sodium Hydrate.*—Sodium hydroxide is a white brittle mass of 2·13 specific gravity; it melts at a low red heat, and is volatilised at high temperatures; it is hygroscopic and deliquescent, exceedingly soluble in water with evolution of heat, and is also soluble in alcohol. The aqueous solution is called caustic soda-lye.

SPECIFIC GRAVITY OF CAUSTIC SODA AT 15° C., PERCENTAGES OF Na_2O and NaOH (*Schiff and Gerlach*).

Per Cent. of the Solution.	Specific Gravity for Na_2O.	Specific Gravity for NaOH.	Per Cent. of the Solution.	Specific Gravity for Na_2O.	Specific Gravity for NaOH.
1	1·015	1·012	31	1·438	1·343
2	1·020	1·023	32	1·450	1·351
3	1·043	1·035	33	1·462	1·363
4	1·058	1·046	34	1·475	1·374
5	1·074	1·059	35	1·488	1·384
6	1·089	1·070	36	1·500	1·395
7	1·104	1·081	37	1·515	1·405
8	1·119	1·092	38	1·530	1·415
9	1·132	1·103	39	1·543	1·426
10	1·145	1·115	40	1·558	1·437
11	1·160	1·126	41	1·570	1·447
12	1·175	1·137	42	1·583	1·456
13	1·190	1·148	43	1·597	1·468
14	1·203	1·159	44	1·610	1·478
15	1·219	1·170	45	1·623	1·488
16	1·233	1·181	46	1·637	1·499
17	1·245	1·192	47	1·650	1·508
18	1·258	1·202	48	1·663	1·519
19	1·270	1·213	49	1·678	1·529
20	1·285	1·225	50	1·690	1·540
21	1·300	1·236	51	1·705	1·550
22	1·315	1·247	52	1·719	1·560
23	1·329	1·258	53	1·730	1·570
24	1·341	1·269	54	1·745	1·580
25	1·355	1·279	55	1·760	1·591
26	1·369	1·290	56	1·770	1·601
27	1·381	1·300	57	1·785	1·611
28	1·395	1·310	58	1·800	1·622
29	1·410	1·321	59	1·815	1·633
30	1·422	1·332	60	1·830	1·643

Sodium hydroxide is a very strong monacid base, being inferior only to potassium hydroxide, and possesses strong caustic properties and a caustic taste. It readily absorbs carbon dioxide from the air to form carbonate of soda. Heat is evolved on mixing strong solutions of caustic soda with water.

Sodium hydroxide is prepared by decomposing sodium carbonate with lime or with ferric oxide (ferrite process), but in greater quantities from rock salt by the Le Blanc process. It is now also prepared in considerable quantities by the electrolysis of sodium chloride. Almost pure caustic soda is now manufactured on a very large scale. The usual *brands of commerce are caustic soda* 48°, 60°, 70°, 74°, 76°, and 77°, each degree indicating 1 per cent. of sodium oxide (Na_2O); caustic soda, 77°, is almost chemically pure sodium hydroxide. The strength of a caustic soda is estimated by titration with standard acid (see *Analysis*), and the strength of a solution is roughly ascertained by the hydrometer (see Table). Of course, the latter method does not give reliable results in the case of the products containing carbonate, sulphate, chloride, &c., of sodium and other salts.

Sodium hydroxide is used in large quantities in the manufacture of soap, paper, and dyestuffs; as well as in bleaching, dyeing, mercerising, and in many other industries.

Sodium Peroxide, Na_2O_2, is manufactured on the large scale by heating sodium in a current of air at 300° C. It possesses a creamy white colour, is deliquescent in the air, and absorbs carbon dioxide, thereby losing oxygen and being converted into sodium carbonate. It dissolves in water with generation of heat and evolution of oxygen. If mixed with ice, however, there is a considerable lowering in temperature, and no oxygen is given off.* In dilute acids, if kept cool, it dissolves without evolution of oxygen, hydrogen peroxide and the corresponding sodium salt being formed.

Sodium peroxide comes into the market as a yellowish-white powder, containing nearly 20 per cent. of available oxygen, whilst the formula Na_2O_2 requires 20·5 per cent.; thus the product is fairly pure. It may be brought into contact with oxidisable substances, like wood or metal, in the dry state, but if the latter be moist or wet there is danger of firing.

Sodium peroxide is used for bleaching goods of all kinds, especially such as are formed of animal fibres and tissues—*e.g.*, silk, tussur, wool, hairs, feathers, and ivory, but also for bleaching cotton goods. Its application, however, owing to its relatively high cost, is limited to the better class of goods.

Sodium Sulphate, Na_2SO_4—*Glauber's Salt,* $Na_2SO_4 + 10H_2O$.—Sodium sulphate is produced by decomposing salt (sodium chloride) with sulphuric acid, hydrochloric acid also being formed—$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$.

Most of the sodium sulphate which is manufactured is converted into soda; the greater part of the remainder is used for glassmaking. Sodium sulphate (without water of crystallisation) is obtained by calcination of crystallised Glauber's salt or by evaporating the solution above 33° C.; it is also called *calcined* (anhydrous) *Glauber's salt.* This salt occurs in rhombic crystals; it is readily soluble in water, but insoluble in alcohol. It attracts water from the atmosphere, thereby becoming moist; but it is not deliquescent. It dissolves at 21·5°, and at higher temperatures in water with evolution of heat; at + 3° and below, with absorption of heat; for this reason it is sometimes mixed with ice or snow in order to produce artificial cold. It crystallises with 7 or 10 molecules of water from solutions below 33° C.

Glauber's Salt or Glaubersalt, $Na_2SO_4 + 10H_2O$, is obtained by crystallisation from solutions at temperatures below 33°, and forms large monoclinic crystals. It contains 44·1 per cent. anhydrous salt and 55·9 per cent. water. In the atmosphere it effloresces, and at 33° it loses its water of crystallisation.

* R. Bauer, *Journ. Soc. Dyers and Col.*, 1906, p. 333.

The term ***sodium sulphate*** is adopted in this work for the calcined Glaubersalt, and *Glaubersalt* for the compound, $Na_2SO_4 + 10H_2O$. They may be substituted for each other in the ratio of 11 calcined to 25 crystallised salt. The commercial products contain more or less sodium chloride, which, for most purposes, is not very objectionable. For the determination of the latter the quantity of chlorine present has to be estimated. The anhydrous salt may contain more sulphuric acid or less than is required by the formula Na_2SO_4. The excess of either acid or alkali can be proved by the reaction on litmus paper, the colour of which is not affected by the normal salt.

Solubility of Sodium Sulphate (Anhydrous Salt, Na_2SO_4) in 100 parts of Water at various temperatures.

0° C.	10° C.	15° C.	20° C.	25° C.	30° C.	33° C.	40° C.	103° C.
Parts. 5	Parts. 9	Parts. 13	Parts. 19	Parts. 28	Parts. 40	Parts. 50	Parts. 49	Parts 42·6

Specific Gravity of Solutions of Anhydrous Sodium Sulphate (Na_2SO_4) at 15° C.

Specific Gravity.	Per Cent. Na_2SO_4.	Specific Gravity.	Per Cent. Na_2SO_4.	Specific Gravity.	Per Cent. Na_2SO_4
1·0091	1	1·0457	5	1·0832	9
1·0182	2	1·0550	6	1·0927	10
1·0274	3	1·0644	7	1·1025	11
1·0365	4	1·0737	8	1·1117 (saturated).	12

Sodium sulphate is largely used by dyers, both in its crystallised and in its calcined form. It is employed in the finishing of cotton goods, and is found in most of the dyestuffs which are sold in the form of powders or pastes, occurring partly as an impurity resulting from the mode of manufacture, and partly as an addition for the purpose of reducing the colours to the usual standards of commerce. It is used by the dyer to regulate the dyeing operations in various capacities.

1. In cotton dyeing it ensures in many cases the more complete exhaustion of the dye-bath, since by decreasing the solubility of the colouring matters it causes them to pass more rapidly into the fibres. Such is the case with the direct cotton colours and sulphide colours, which are taken up by the cotton fibre more completely from concentrated than from dilute solutions. Other neutral salts, such as sodium chloride, will produce the same effect.

2. In wool dyeing, sodium sulphate has the opposite effect. From dyed wool it strips the colour until an equilibrium has been established.* By redissolving the colour on the fibre it may thus assist levelling.

3. Sulphuric acid forms, with sodium sulphate, sodium bisulphate, and this compound has a less energetic acidifying action than the free sulphuric acid. The acid dyestuffs, therefore, are more slowly attracted by the fibre in the presence of Glaubersalt, and, consequently, they then dye more evenly; moreover, they are not retained by the surface so much, but penetrate deeper into the fibre, thus dyeing it better through. For this reason most of the acid colours dye much better with the addition of Glaubersalt to the dye-bath in amounts varying from $2\frac{1}{2}$ to 10 per cent.

* A. W. Hallitt, "The Theory of the Acid Dye-bath," *Journ. Soc. Dyers and Col.*, 1899, p. 30; E. Knecht, *ibid.*, 1905, p. 250.

4. In the case of it being desirable for shading to dye colours in an acid-bath which are not readily attracted by the fibre in the presence of an acid, sodium sulphate has a similar neutralising effect as in the former case, and enables the fibre to absorb such a colour (for instance, a basic colour) without preventing the dyeing of the acid dyestuff.

The amounts of Glaubersalt which give the best results vary according to the class of colouring matter employed. In cotton dyeing they are generally far greater than in wool dyeing. It should, however, be borne in mind that most dyestuffs are more or less completely "salted out" or mechanically precipitated by a large excess of Glaubersalt, and that there is a limit to its use, especially as an addition to the bath in the dyeing of direct colours on cotton. For if the amount taken is sufficient to salt out the dyestuff, uneven dyeing is almost sure to result. In case, however, it should be desirable, for reasons of economy, to exhaust the dye-bath as completely as possible, only a portion of the Glaubersalt is added at the commencement of the dyeing operation, the rest being added in either one or in two portions as the dyeing proceeds. Glaubersalt constitutes the best means of partly stripping, and at the same time levelling, many of the acid colours dyed on wool.

In all these cases, of course, it makes little difference whether calcined or crystallised Glauber's salt is used, provided equivalent quantities are taken.

Acid Sodium Sulphate, $NaHSO_4$.—*Bisulphate of Soda.*—This salt, which is obtained by combining equal molecular weights of sodium sulphate and sulphuric acid, is frequently offered to the trade as *tartar substitute* and under similar fancy names. It crystallises both in the anhydrous state and with 1 molecule of water of crystallisation, and is very soluble in water. The diluted aqueous solution of the salt decomposes into sulphuric acid and sodium sulphate. Acid sodium sulphate is used as a mild acidifying agent, similar to a mixture of sulphuric acid and sodium sulphate as described above. Practical dyers state that the acid sulphate acts better than the mixture of the normal sulphate and sulphuric acid; this can be explained by the fact that the acid and normal salts do not readily combine in aqueous solutions, and that the acid remains in the free state, while it is liberated gradually when added in the form of the acid sulphate.

Sodium Sulphite, $Na_2SO_3 + 7H_2O$.—Sodium sulphite is obtained by the action of sulphur dioxide on a solution of sodium carbonate. It crystallises in monoclinic prisms which contain exactly 50 per cent. of water. It is fairly soluble in water, and not hygroscopic; when the solution is heated the anhydrous salt (Na_2SO_3) is separated. Sodium sulphite oxidises in the air and forms sodium sulphate.

The commercial product contains more or less sulphate, as also carbonate; it should contain over 22 per cent. sulphur dioxide, which is estimated by the methods given for this compound.

Sodium Bisulphite, $NaHSO_3$.—Sodium bisulphite is manufactured by saturating a hot solution of sodium carbonate with sulphur dioxide, and allowing the product to crystallise. It forms white crystals which smell of sulphur dioxide, owing to liberation of that gas, and change to sodium sulphate by slow oxidation. A very similar product is *sodium metasulphite* ($Na_2S_2O_5$). Both are expensive products, and retain their original strength (about 62 and 66 per cent. respectively of SO_2) for a short time only. Generally the solution of sodium bisulphite is used (*bisulphite of soda*) which does not change in well closed wooden casks. As sold its specific gravity varies from 1·26 to 1·40 (52° to 80° Tw.). A solution heavier than 1·31 (62° Tw.) is liable to deposit crystals of bisulphite in very cold weather, which fact is not always noticed. A bisulphite of soda solution of the strength 52° to 62° Tw. should contain 20 to 23 per cent. sulphur dioxide (SO_2), be clear and nearly colourless, and

smell of sulphur dioxide. Sodium bisulphite is used in the bleaching of wool and silk, for the preparation of sodium hydrosulphite, for rendering certain dyestuffs soluble (coeruleïn), as an antichlor, and for other purposes.

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM BISULPHITE AT 15° (*Chemiker-Kalender*).

Specific Gravity.	Per Cent. $NaHSO_3$.	Per Cent. SO_2.	Specific Gravity.	Per Cent. $NaHSO_3$.	Per Cent SO_2.
1·008	1·6	0·4	1·171	16·5	10·2
1·022	2·1	1·3	1·190	18·5	11·5
1 038	3·6	2·2	1·210	20·9	12·9
1·052	5·1	3·1	1·230	23·5	14·5
1·068	6·5	3·9	1·252	25 9	15 9
1·084	8·0	4·8	1 275	28·9	17·8
1·100	9·5	5·7	1·298	31·7	19·6
1·116	11·2	6·8	1·321	34·7	22·5
1·134	12 8	7·8	1·345	38·0	23·6
1·152	14·6	9·0			

Sodium Thiosulphate, $Na_2S_2O_3 + 5H_2O$—*Hyposulphite of Soda, Antichlor.*—Sodium thiosulphate, commonly known as hyposulphite of soda, is obtained from alkali waste. It is a very soluble and slightly deliquescent salt. Hydrochloric acid decomposes the aqueous solution, sulphur being separated in a finely divided state, and sulphur dioxide given off.

Sodium thiosulphate evinces strong reducing properties. It reacts with the halogens and transforms them into compounds with sodium; the reaction with iodine proceeds according to the equation—$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$. On this reaction is based the use of sodium thiosulphate in volumetric analysis. Chlorine reacts similarly to iodine with sodium thiosulphate. (See below.)

Commercial sodium thiosulphate is almost chemically pure. It is used sometimes as a mordant for wool, and finds application as an antichlor in the treatment of vegetable fibres after they have been bleached with a hypochlorite—*i.e.*, it transforms free chlorine into a non-oxidising compound, as indicated above.

Sodium Hydrosulphite, $Na_2S_2O_4$—*Schuetzenberger's salt.*—This salt is now manufactured in the anhydrous state by the Badische Anilin- und Soda-Fabrik,* and the Farbwerke, Hoechst (M.L.B.), but is usually prepared by dyers who use it for the reduction of indigo (*Hydrosulphite vat*) and other vat colours.

Sulphurous acid is reduced by zinc or iron to *hydrosulphurous acid*, which dissolves in water with a yellow colour, and is extremely unstable, decomposing within a few minutes at the ordinary temperature, with simultaneous deposition of free sulphur.

Hydrosulphurous acid is a far more powerful reducing agent than sulphurous acid. The sodium salt is obtained by the reduction of sodium bisulphite (in strong solution) with zinc in the form of zinc-dust, or better, zinc-clippings (to avoid too great an evolution of heat); the liquid must be kept cool. The zinc sodium sulphite separates in the form of crystals, while the sodium hydrosulphite remains in solution as long as the liquor is warm. The latter salt is not a stable compound in the presence of water, it readily takes up oxygen from the air to form sodium sulphite; and in the absence of air it soon decomposes in aqueous solution, forming sodium thiosulphate For this reason, only such quantities as are required for immediate use should be prepared. The dehydrated salt is, however, a very stable substance.

* English Patent 7,397, 1904, *Journ. Soc. Dyers and Col.*, 1905, p. 114.

According to Bernthsen,* the first stage of the reaction takes place according to the equation—$Zn + 4NaHSO_3 = ZnSO_3 + Na_2SO_3 + Na_2S_2O_4 + 2H_2O$. On allowing to stand, it is found, however, that a larger proportion of bisulphite is reduced than would correspond to this equation. The complete reaction is shown by the following equation—$3Zn + 10NaHSO_3 = Zn_3Na_2S_3O_{10} + Na_2SO_3 + 3Na_2S_2O_4 + 5H_2O$. The more dilute the solution of bisulphite employed, the slower will the reaction be. Thus, whereas with a solution containing 0·5852 grm. $NaHSO_3$ in 1 litre, the maximum amount of hydrosulphite was only formed in 265 hours, a solution containing 26·97 grms. in 1 litre reached a maximum in 1½ hours.

The practical preparation of hydrosulphite is described under indigo (*q.v.*).

Sodium Sulphoxylate - Formaldehyde — $HO . CH_2 . O . SO . Na, 2H_2O = NaHSO_2 + CH_2O + 2H_2O$—*Hydrosulphite N F Extra* (M.L.B.)—*Hyraldite C Extra* (Cassella)—*Rongalite C* (B.A.S.F.).—By the action of formaldehyde on sodium hydrosulphite a very stable product is obtained according to the following equation :—

$$(Na_2S_2O_4 . 2H_2O) + 2CH_2O + 2H_2O = (NaHSO_2 . CH_2O . H_2O) + (NaHSO_3 . CH_2O . 2H_2O).$$

The product is thus a molecular mixture of the formaldehyde compounds of *sodium sulphoxylate*, $NaHSO_2$ (a salt not yet obtained in the free state), and of sodium bisulphite. The pure formaldehyde compound of sodium sulphoxylate separates from the aqueous solution in clinorhombic crystals, which correspond to the formula $NaHSO_2 . CH_2O . 2H_2O$, and is prepared on the large scale by reducing sulphurous acid with zinc dust in the presence of formaldehyde at an elevated temperature and in the presence of acid.†

In contrast with the hydrosulphites the formaldehyde compounds of these and of the sulphoxylates exert their very strong reducing power only at an elevated temperature or when dissociated by acids. They do not readily oxidise in the air, and, therefore, they may be kept in store for a considerable time, if protected against heat and moisture.

The commercial products form greyish-white lumps, and are used in very large quantities in the textile printing industry for discharging reducible colours, especially azocolours, on the various fibres, and also for stripping dyed goods.

For the latter purpose the *Formaldehyde compound of Basic Zinc Sulphoxylate* (which is marketed under the denomination of *Decroline, Hyraldite Z for stripping, Hydrosulphite A Z*) is preferred. This compound forms a grey stable substance, insoluble in water, but soluble in dilute acids, and exerts, on dissolving a powerful reducing and stripping action (see Part vii., *Acid Colours*).

Sodium Chloride, NaCl—*Common Salt, Rock Salt, Salt.*—Sodium chloride and its sources are well known. It forms crystals of the regular system, without water of crystallisation, melts at 776°, and is volatilised at a white heat. On being heated, the ordinary salt decrepitates, owing to mechanically enclosed moisture. The solubility of sodium chloride is nearly the same at different temperatures; 100 parts of water dissolve, according to Poggiale, at—

0° C.	15° C.	25° C.	40° C.	60° C.	80° C.	100° C.
Parts. 35·5	Parts. 35·9	Parts. 36·1	Parts. 36·6	Parts. 37·3	Parts. 38·2	Parts. 39·2

* A. Bernthsen, *Lieb. Ann.*, 208, p. 148; see also *Berl. Ber.*, 1905, p. 1048; M. Bazlen, *Berl. Ber.*, 1905, p. 1057; *Journ. Soc. Dyers and Col.*, 1905, p. 140.

† L. Baumann, G. Thesmar, and J. Frossard, *Journ. Soc. Dyers and Col.*, 1905, p. 14; M. Bazlen, *ib.*, p. 140. English Patents 5,867 and 19,446 of 1903, 13,955 of 1904, &c.

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM CARBONATE AT 23° (*Schiff*).*

Specific Gravity.	Per Cent. $Na_2CO_3 + 10H_2O$.	Per Cent. Na_2CO_3.	Specific Gravity.	Per Cent. $Na_2CO_3 + 10H_2O$.	Per Cent. Na_2CO_3.
1·0038	1	0·370	1·1035	26	9·635
1·0076	2	0·741	1·1076	27	10·005
1·0114	3	1·112	1·1117	28	10·376
1·0153	4	1·482	1·1158	29	10·746
1·0192	5	1·853	1·1200	30	11·118
1·0231	6	2·223	1·1242	31	11·488
1·0270	7	2·594	1·1284	32	11·859
1·0309	8	2·965	1·1326	33	12·230
1·0348	9	3·335	1·1368	34	12·600
1·0388	10	3·706	1·1410	35	12·971
1·0428	11	4·076	1·1452	36	13·341
1·0468	12	4·447	1·1494	37	13·712
1·0508	13	4·817	1·1536	38	14·082
1·0548	14	5·188	1·1578	39	14·453
1·0588	15	5·558	1·1620	40	14·824
1·0628	16	5·929	1·1662	41	15·195
1·0668	17	6·299	1·1704	42	15·566
1·0708	18	6·670	1·1746	43	15·936
1·0748	19	7·041	1·1788	44	16·307
1·0789	20	7·412	1·1830	45	16·677
1·0830	21	7·782	1·1873	46	17·048
1·0871	22	8·153	1·1916	47	17·418
1·0912	23	8·523	1·1959	48	17·789
1·0953	24	8·894	1·2002	49	18·159
1·0994	25	9·264	1·2045	50	18·530

Sodium Hypochlorite, $NaClO$—*Eau de Labarraque, Chloride of Soda.*—Sodium hypochlorite is most conveniently prepared by grinding bleaching powder with a solution of soda, when it is formed by double decomposition, $CaOCl_2 + Na_2CO_3 = NaOCl + NaCl + CaCO_3$. It is also made on the large scale by saturating a solution of caustic soda with chlorine, and sometimes by means of electrolysis of common salt brine, and employed in the place of chloride of lime, over which it has the advantage of not forming precipitates of sulphate or carbonate of calcium in the material to be bleached.

Sodium Chlorate, $NaClO_3$.—Sodium chlorate has the same general properties as potassium chlorate, and has replaced the latter almost entirely in dyeing and printing owing to its greater solubility and lower price. It dissolves in its own weight of cold and half its weight of hot water. The process of manufacture is similar to that of potassium chlorate.

Sodium Chromate and Bichromate (see *Chromium*).

Sodium Ferrocyanide, $Na_8Fe_2(CN)_{12} + 24H_2O$, resembles the potassium salt, but contains more water of crystallisation.

Sodium Ferricyanide, $Na_6Fe_2(CN)_{12} + H_2O$, is also very similar to the potassium salt. It dissolves in 1·25 parts of boiling or in 5·3 parts of cold water, and is deliquescent in the atmosphere.

Sodium Arsenate, $Na_2HAsO_4 + 12H_2O$—*Arsenate of Soda*—**Sodium Binarsenate,** $NaH_2AsO_4 + H_2O$.—Arsenate of soda is obtained by evaporating a solution of arsenic in soda with the addition of sodium nitrate to dryness and heating the mass. The commercial product occurs either in crystals or in white masses, and has a greatly varying composition, containing from 30 to 60

* The temperature of 23° has been selected, because strong liquors of sodium carbonate would separate crystals at 15°.

per cent. arsenic acid (As_2O_5) and considerable quantities of common salt. It consists principally of the two above-named arsenates of sodium. A solution of the salt is also a commercial article.

Sodium arsenate is extensively used as a fixing agent for mordants, and as a substitute for cow-dung in the so-called operation of "dunging" or "fixing." Its action consists in converting certain metallic mordants, especially aluminium and iron salts, into insoluble arsenates, and thus fixing them permanently. In calico printing, sodium arsenate also prevents the loosely-adhering excess of mordant from being absorbed by those spots of the piece which should remain white, by making this excess insoluble, and therefore non-absorbable. It is especially used for the purpose of keeping the whites of print goods clear. In yarn dyeing, it affects the hands of the workmen owing to its poisonous properties. As it is so dangerous both to the workmen and to all who handle the dyed goods, while the neighbouring streams are liable to be contaminated with arsenical liquor, its use is objectionable; hence, in some countries, this has been prohibited. Minute quantities of arsenic remain in the finished goods, and may give rise to cases of poisoning, which, however, are very rare.

Sodium Phosphate, $Na_2HPO_4 + 12H_2O$—*Phosphate of Soda.*—This salt is found in commerce in the form of monoclinic crystals, which dissolve sparingly in cold water (1 in 25 at 10° C.), but readily in hot water (1 in 1 at 100° C.). The salt effloresces in the air. The commercial product often contains sodium sulphate.

Sodium phosphate is used as a substitute for the arsenate in fixing aluminium and iron mordants. It does not act, however, so well as the arsenate, because aluminium phosphate is not insoluble under certain conditions. Liechti and Suida* state that sodium phosphate does not produce a precipitate in a large excess of aluminium sulphate; two equivalents of $Al_2(SO_4)_3$ are necessary to retain one equivalent, $AlPO_4$, in solution. The high price of sodium phosphate also prevents it from being extensively used.

Sodium Tetrasilicate, $Na_2Si_4O_9$—*Silicate of Soda.*—This compound is obtained by melting sand with soda ash and charcoal. It is met with in commerce under the name of *soluble glass*, either as a more or less coloured vitreous mass, or as a thick aqueous solution. The substance is very soluble in water, but it is not deliquescent in the air. The aqueous solution dissociates into acid and basic salts when diluted. Sodium silicate acts as a mild alkali; the commercial article sometimes contains a considerable excess of caustic alkali. The aqueous solution is decomposed by carbon dioxide from the air, and should be kept in well-closed vessels.

Sodium silicate was first prepared by Fuchs for the preservation of "fresco-paintings," and is still used for this purpose. Textile goods, stage decorations, light dresses, or curtains are impregnated with sodium silicate to prevent them from taking fire. Soap is "filled" with the substance to lower the cost of manufacture; and the addition should not be regarded entirely as an adulteration, since silicate of soda has, like soap, detergent properties. It is also used alone in bleaching, acting as a mild alkali. For certain dyestuffs (for instance, for Aniline green) silicic acid in a finely-divided state serves as a mordant, and is produced on the fibre by saturating the goods with a solution of sodium silicate, and passing them through a weak acid. Sodium silicate serves also as a fixing agent for metallic mordants like the arsenate and phosphate, especially of iron and chromium. Aluminium salts treated with sodium silicate do not readily attract the colouring matter from the dye-bath, and do not yield such bright shades as when fixed by the arsenate. This is owing to the fact that silicic

* *Journ. Soc. Chem. Ind.*, 1883, p. 537.

acid, being a very weak acid, does not readily combine with the aluminium hydroxide, so that the precipitation of the latter is more or less prevented by the basic silicates, which are generated by dissociation (see above). Besides, the commercial product contains an excess of caustic soda, which would cause the removal of the mordant from the fibre in the form of a soluble aluminate of sodium. Iron and chromium oxides, on the other hand, which are not soluble in the alkali, are well fixed by sodium silicate.

Sodium Pyroborate, $Na_2B_2O_7 + 10H_2O$—*Borax.*—This salt forms monoclinic prisms; or, in the anhydrous state ($Na_2B_2O_7$), a white powder. The crystals dissolve in about twenty times their weight of cold, and half their weight of hot water

Borax is used in the laundry, the laboratory, and as a mild alkali in the dyeing of some direct cotton colours on cotton, and of Alkali blues on wool.

Sodium Acetate, $NaC_2H_3O_2 + 3H_2O$—*Acetate of Soda.*—The salt forms crystals which lose their water of crystallisation in the air; they readily dissolve in water (1 part in 3·9 parts of water at 6° C.).

Sodium acetate is used to transform free mineral acids into their sodium salts, with liberation of an equivalent amount of acetic acid in cases where the presence of the former in the free state would prevent certain chemical reactions; or where they might tender the textile fibres, and where acetic acid would produce neither of these effects. For the former reason sodium acetate is added to the diazocompounds in developing azocolours on the fibre.

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM ACETATE AT 17·5° (*Franz*).

Per cent. $NaC_2H_3O_2$	Specific Gravity.	Per cent. $NaC_2H_3O_2$.	Specific Gravity.
5	1·0292	20	1·1074
10	1·0538	25	1·1374
15	1·0[illegible]02	30	1·1706

SOAP.

Vegetable and animal oils and fats consist for the most part of the glycerides of the higher fatty acids. Sperm and a few other similar oils are exceptions. They contain, in place of the radical of glycerin, solid monatomic alcohols, which are also combined with fatty acids.

Glycerides, when treated under suitable conditions with strong bases, are decomposed, glycerin is liberated, and salts of the fatty acids are formed. All such salts, in the widest sense, are "soaps."

In the ordinary sense, however, *soap* is understood to refer to the compounds formed by the action of fatty acids or their glycerides upon the bases *potash* and *soda* only. These are soluble in water, all others (excepting ammonia soaps, which are not of much practical importance) are insoluble. Resin or colophony, which contains pinic, sylvic, abietic, and other acids, also forms soaps with the alkalies. Rosin soap is not often used alone, but it enters largely into the composition of yellow household soaps. Excepting its use in bleaching calico for printing, soap containing resin is objectionable for general use in textile industries.

The most commonly occurring fatty acids in soaps are those obtained by the saponification of lard and tallow—viz., stearic, palmitic, and oleïc acids. In addition to these, soaps frequently contain the following fatty acids:—Lauric

acid, from cocoa-nut oil; brassic acid, from rape oil; linoleic acid, from linseed and other drying oils; and occasionally ricinoleic acid, from castor oil.

The fatty acids are monobasic acids, whereas glycerin, the radical of which is combined with the fatty acids in neutral oils and fats, plays the part of a tri-acid base. It is a tri-hydric alcohol. When oils and fats are boiled with potash or soda, saponification takes place, three molecules of alkali being required to displace one of glycerin. For example, stearin, which is glycyl tristearate (the chief constituent of mutton fat), undergoes the following change when boiled with caustic potash:—

$$\underset{\text{Stearin.}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{Potash}}{3KHO} = \underset{\text{Glycerin.}}{C_3H_5(HO)_3} + \underset{\text{Potassium Stearate (Soap).}}{3KC_{18}H_{35}O_2}.$$

$$890 + 168 = 92 + 966$$

In this reaction 890 parts of stearin are decomposed by 168 parts of caustic potash, with the formation of 966 parts of anhydrous soap.

If palmitin or glycyl tri-palmitate (the chief constituent of palm oil) be treated in like manner a similar reaction takes place; but, on account of the difference in molecular weights, the quantities are different, as shown by the following equation:—

$$\underset{\text{Palmitin.}}{C_3H_5(C_{16}H_{31}O_2)_3} + \underset{\text{Potash.}}{3KHO} = \underset{\text{Glycerin.}}{C_3H_5(HO)_3} + \underset{\text{Potassium Palmitate (Soap).}}{3KC_{16}H_{31}O_2}.$$

$$806 + 168 = 92 + 882$$

In this case 168 parts of potash decompose only 806 parts of fat (palmitin), with the production of 882 parts of anhydrous soap. And according to the glycerides present in oils or fats, more or less potash is required to effect saponification of a given weight of fatty matter. This may be expressed in two ways—either by the amount of caustic potash required to saponify 100 parts of fatty matter, or the amount of oil or fat saponified by one equivalent of potash or soda. In the latter case the figure represents the "saponification equivalent" of the oil or fat. It is the quantity of oil or fat which is saponified by 56 parts of caustic potash, or 40 parts of caustic soda, and may be obtained by dividing the percentage of caustic potash required for saponification into 5,600, or the percentage of caustic soda into 4,000. In the case of fatty acids the saponification equivalents are identical with their molecular weights (fatty acids being monobasic), whereas with the tri-glycerides or neutral fats and oils the saponification equivalents are one-third of their molecular weight.

The table on next page shows the saponification equivalenes of the more important fatty acids, glycerides, natural oils and fats.

Natural oils from the same sources have not always exactly the same composition. They are not chemical compounds, but mixtures of several compounds—the glycerides. The majority of fixed oils on saponification yield from 95 to 96 per cent. of fatty acids, and about 10 per cent. of glycerin. Fats containing much lauric acid give rather different results. The following table contains a few examples of the theoretical proportions of fatty acid and glycerin, resulting from the saponification of pure tri-glycerides:—

	100 Parts of Glyceride yield	
	Fatty Acid.	Glycerin.
Laurin, ...	94·04	14·42
Palmitin, ...	95·28	11·41
Stearin, ...	95 73	10·34
Olein, ...	95·70	10·40
Brassein, ...	96·39	8·75
Linolein, ...	95·21	11·68
Ricinolein, ...	95·92	9·88

The increase in weight is due to what is termed "hydrolysis." On saponification the elements of water are taken up to form glycerin, and on decomposing the soap with a mineral acid water also takes part in the reaction to form the fatty acids.

Fatty Body.		Percentage of Potash (KHO) for Saponification.	Saponification Equivalent.
Lauric acid,	$C_{12}H_{24}O_2$,	28	200
Palmitic acid,	$C_{16}H_{32}O_2$,	21·88	256
Stearic acid,	$C_{18}H_{36}O_2$,	19·72	284
Oleic acid,	$C_{18}H_{34}O_2$,	19·85	282
Brassic acid,	$C_{22}H_{42}O_2$,	16·57	338
Linoleic acid,	$C_{16}H_{28}O_2$,	22·22	252
Ricinoleic acid,	$C_{18}H_{34}O_3$,	18·79	298
Laurin,	$C_3H_5(C_{12}H_{23}O_2)_3$,	26·38	212·7
Palmitin,	$C_3H_5(C_{16}H_{31}O_2)_3$,	20·88	268·7
Stearin,	$C_3H_5(C_{18}H_{35}O_2)_3$,	18·91	296·7
Olein,	$C_3H_5(C_{18}H_{33}O_2)_3$,	19·04	294·7
Brassein,	$C_3H_5(C_{22}H_{41}O_2)_3$,	16·00	350·7
Linolein,	$C_3H_5(C_{16}H_{27}O_2)_3$,	21·20	264·7
Ricinolein,	$C_3H_5(C_{18}H_{33}O_3)_3$,	18·06	310·7
Olive oil,		19 to 19·5	287 to 295
Cotton-seed oil,		19·1 to 19·7	284 to 293
Rape oil,		17 to 17·6	318 to 330
Linseed oil,		18·7 to 19·5	287 to 300
Palm oil,		19·6 to 20·2	277 to 285
Cocoa-nut oil,		24·6 to 26·8	208 to 228
Tallow,		19·3 to 19·8	283 to 290
Castor oil,		17·6 to 18·1	310 to 319

As a rule, the higher the solidification point of an oil or fat, the greater is the consistency of the soap made from it with the same alkali.

Soda forms much harder and firmer soaps than potash. In fact, all ordinary so-called *hard* soaps contain soda as the base, while *soft* soaps (often called "sweet" soaps) contain potash as the base. The hardest commercial soaps are those made with soda and fatty matter containing much stearic acid, such as tallow; and the softest are those made with potash and oils containing principally olein, linolein, or ricinolein. Potash soaps are highly deliquescent; according to Lant Carpenter, 100 parts of potassium oleate exposed to air absorb 162 parts of water, and 100 parts of potassium palmitate absorb 35 parts, whereas 100 parts of dry sodium stearate absorb only 7½ parts. These quantities, of course, are liable to vary according to the conditions of the atmosphere, but they show comparative results.

Some soaps, notably those made with cocoa-nut oil, have a remarkable property of retaining a very high percentage of water (70 to 80 per cent.) and still remaining fairly hard.

Soaps are insoluble in solutions of alkaline salts, and also in strong solutions of caustic alkali; hence, in the process of manufacture the potash or soda used must not be more than of a certain strength, otherwise the partially formed soap will be thrown out of solution. On the addition of common salt to a solution of soda soap, the latter separates out as a curdy mass and rises to the surface. This property is utilised on the large scale for separating the

soap from excess of alkali and impurities in the "lye" employed. The glycerin liberated by the decomposition of the fatty matter also remains in the alkaline solution. The operation is usually termed "salting out." For the production of a pure neutral "curd" soap, the solution is run off, the soap dissolved in a fresh quantity of water, and the operation of salting out repeated.

When common salt is added to a solution of potash soap a double decomposition takes place, resulting in the production of a soda soap with formation of potassium chloride. In England, potash soaps are not "salted out;" hence, "soft" soaps made with neutral oils and fats invariably contain glycerin and usually excess of alkali. In some parts of the Continent where potassium chloride is abundant, this salt is used for the production of a neutral potash soap.

For details of manufacture, works such as W. Lant Carpenter's *Soap Candles, &c.*, and Richardson and Watt's *Chemical Technology*, should be consulted. We shall only give here a brief outline. The methods employed for producing soap may be broadly classified as follows:—

I. By the direct saponification of fatty acids by caustic or carbonated alkalies.

II. By saponifying neutral oils and fats (glycerides) in the cold with exact quantities of strong solutions of caustic alkali.

III. By boiling oils and fats in large open vessels with comparatively weak solutions of caustic alkali, with subsequent concentration to a semi-solid mass.

IV. By boiling as in class 3 (but using caustic soda only), with subsequent "salting out" and elimination of the glycerin.

The first three processes are used for both potash and soda soaps. Soaps made according to methods I. and IV. contain no glycerin unless added direct. Those made by methods II. and III. retain the glycerin formed during saponification.

Method I.—The fatty acids employed are almost exclusively those obtained as a bye-product in the manufacture of stearic and palmitic acids for candles. The liquid portion known as "red oil" and "oleine" consists essentially of oleic acid, with small quantities of stearic and palmitic acids. When prepared by the autoclave process, the product often contains more or less undecomposed glycerides as well as small quantities of hydrocarbon oils. If glycerides are present in notable proportions, it is best to saponify with caustic alkalies. Large quantities of soap, however, are made from "oleine" and potassium or sodium carbonate for washing raw wool, yarn, and cloth.

A solution of potash soap suitable for washing wool may be readily obtained by boiling 100 lbs. "oleine" and 25 to 30 lbs. of pure potassium carbonate (or an equivalent amount of commercial pearl ashes) with about 100 gallons of water in a large iron tank; 25 lbs. of potassium carbonate are required to produce a neutral soap, but for most kinds of work at least 30 lbs. may be used with advantage. A potash soap is admittedly superior to a soda soap for washing wool and woollen fabrics, but on account of cheapness soda is more frequently employed—especially for low class-goods. To produce a neutral soda soap with 100 lbs. of "oleine," about 19 lbs. of pure sodium carbonate are required, but in practice at least 25 lbs. are usually taken.

"Oleine," in addition to its direct use, is also largely employed in conjunction with other oils and fats for making soaps by the third process.

The following table (pp. 208, 209), compiled principally from Allen's *Commercial Organic Analysis*, shows the origin and chief properties of the more important oils and fats (with oleic acid and resin) used in the manufacture of soap:—

Name of Oil.	Source.	Chief Components of Oil.	Specific Gravity at 15·5° C.	Solidification point °C.	Saponification equivalent.	Lbs. of pure caustic potash required to saponify 100 lbs of oil.	Lbs of pure caustic soda required to saponify 100 lbs. of oil.	Other Characters, &c.
A. *Of Animal Origin:*								
Bone Fat, . .	Bones of various animals.	Olein and palmitin.	·915	......	284 to 293	19·1 to 19·7	13·6 to 14·1	Brownish colour; unpleasant smell. May contain calcium phosphate.
Lard, ...	From abdomen and other parts of the pig.	Olein, palmitin and stearin.	·860 to ·863*	27 to 44	286 to 292	19·2 to 19·6	13·7 to 14	Varies greatly in composition.
Lard Oil, . .	Obtained by pressing lard.	Olein.	·915	−4 to +10	290	19·3	13·8	Soluble in an equal weight of boiling alcohol. Gives a firm "elaiden."
Tallow, . . .	From the ox and sheep.	Stearin, palmitin, and olein.	·860 to ·863*	33 to 48	283 to 290	19·3 to 19·8	13·8 to 14·2	Varies greatly in composition.
Tallow Oil, . .	Obtained by pressing tallow.	Olein.	·916	0 to 6	288 to 292	19·2 to 19·4	13·7 to 13·9	Much resembles lard oil.
Whale Oil, . .	Blubber of *Balæna mysticetus* and various allied species.	Olein (valerin).	·920 to ·931	......	250 to 296	18·9 to 22·4	13·5 to 16	Yellow or brown colour; disagreeable fishy smell. Gives a pasty "elaiden."
B. *Of Vegetable Origin:*								
Castor Oil, . .	Seeds of *Ricinus communis*.	Ricinolein.	·950 to ·970	−18	310 to 319	17·3 to 18·1	12·6 to 13·1	Very viscous. Readily soluble in alcohol.
Cocoa-nut Oil, .	Nuts of *Cocos nucifera* and *butyracea*.	Laurin, palmitin, and stearin.	·868 to ·874*	16 to 18	208 to 228	24·6 to 26·8	17·6 to 19·2	Consistency of butter. Largely used for making "marine" soap.
Cotton-seed Oil,	Seed of *Gossypium barbadense* and allied species.	Olein and stearin (linolein).	·922 to ·930	1 to 4	284 to 293	19·1 to 19·7	13·6 to 14·1	Gives a pasty "elaiden." Fatty acids have a high melting point—viz., 38° C.

Earth-nut Oil, .	Nuts of *Arachis hypogea.*	Olein, palmitin, arachidin	·916 to ·920	−5	289	19·3	13·8	Gives a firm "elaiden." Resembles olive oil, but contains glycerides of arachidic and hypogeic acids.
Hempseed Oil, .	Seed of *Cannabis sativa.*	Linolein.	·925 to ·931	−15 to −28	290	19·3	13·8	Similar to linseed oil.
Linseed Oil,. .	Seed of *Linum usitatissimum.*	Linolein.	·930 to ·937	−20 to −27	287 to 300	18·7 to 19·5	13·3 to 13·9	Remains liquid when treated with nitrous acid.
Niger-seed Oil,	Seed of *Guizotia oleifera.*	Linolein.	·924 to ·928	Below −9	289 to 295	18·9 to 19·4	1[illegible]·5 to 13·8	Similar to linseed oil.
Olive Oil, . .	Fruit of *Olea Europæa.*	Olein.	·914 to ·917	−6 to +4	287 to 295	19 to 19·5	13·6 to 13·9	Gives a solid "elaiden" of a pale yellow colour.
Palm Oil, . .	Fruit of *Avoira elais.*	Palmitin and olein.	·857 to ·859*	20 to 36	277 to 285	19·6 to 20·2	14 to 14·4	Varies greatly in composition; often contains much free palmitic acid.
Rape-seed Oil, .	Seed of *Brassica campestris*, &c.	Brassein.	·914 to ·916	−6 to −10	318 to 330	17 to 17·6	12·2 to 12·6	Gives a soft "elaiden."
Sesamé Oil, . .	Seeds of *Sesamum indicum.*	Olein.	·921 to 924	−5 to +5	292 to 296	18·9 to 19·2	13·5 to 13·7	Gives a pasty "elaiden."
Oleic Acid or "**Oleine**," .	By pressing mixed fatty acids from tallow and palm oil (candles).	Oleic acid.	·887 to ·908	6 to 22	281 to 293	19·1 to 19·9	13·6 to 14 2	Varies greatly in composition; frequently contains glycerides as well as hydrocarbon oils.
Resin or **Colophony**, . . .	Residue from distillation of crude turpentine.	Abietic acid, &c.	1·04 to 1·10	135	290 to 330	17 to 19·3	12·2 to 13·8	Used only in conjunction with other oils and fats, for yellow household soaps and sometimes for soft soaps.

* The specific gravity of these fats is taken at 98° to 99° C

Method II.—In making soaps by the "cold process," the greatest care must be taken to employ the exact amount of caustic alkali required for saponification. The alkali used must also be pure and free from carbonate. This method is often employed for the manufacture of the cheaper kinds of toilet-soap, and of late years a considerable amount has been made for scouring purposes in the textile industries.

The following quantities are recommended for making a good potash soap by the "cold process" for washing wool:—50 lbs. of good caustic potash are dissolved in 5 gallons of water and allowed to cool. The solution is then gradually poured into a vessel containing 200 lbs. of Gallipoli olive oil during constant stirring with a flat wooden stirrer about 3 inches broad. The stirring is continued until the oil and potash have become thoroughly mixed, when the vessel is covered and put in a warm place for a day or two. The combination between the oil and alkali commences a short time after mixing, and is accompanied by a considerable elevation of temperature.

The above quantities give an almost neutral soap. For anything but the finest work the amount of oil may be reduced to 180 lbs. It is preferable, however, to make a neutral soap and afterwards treat it with refined pearl ashes (potassium carbonate) in the proportion of 1 to 3 per cent.

In place of olive oil, cotton-seed oil, &c., or mixtures of these oils, may, of course, be used.

If it is desired to give the appearance of "figs" to the soap, a little tallow is used in place of a portion of the oil. A neutral hard soda soap may be obtained in the following manner:—150 lbs. of tallow, palm oil, or cocoa-nut oil are melted and brought to a temperature not exceeding 40° C., and a solution of 20 lbs. of pure caustic soda dissolved in 75 lbs. of water at a temperature of about 22° C. gradually added during constant stirring. The mixture is then poured into a soap frame, covered up, and put in a warm place for a few days.

Method III.—Soft soaps are most usually made by boiling olive, cotton seed, linseed, rape seed, hemp seed, and other oils, or mixtures of these oils, with caustic potash lye. The oil is run into the "pan" to the extent of about one-fourth of its capacity, and the requisite amount of a solution of caustic potash (containing a little carbonate) of specific gravity 1·065 to 1·08 (13° to 16° Tw.) added at the same time. The mass is boiled for some hours until saponification has taken place, the completion being determined by the appearance which small samples present when allowed to cool on glass plates. If more alkali is required, a solution of caustic potash, ranging from 1·12 to 1·2 specific gravity (24° to 40° Tw.), is gradually and cautiously added, and the boiling continued. The direct steam (if used) is then turned off and a portion of the water evaporated by boiling with fire or "close" steam only. The finished soap is then run into casks while still hot.

"Hydrated" soda soaps are made in much the same manner as "soft" potash soaps, using an equivalent amount of caustic soda lye in place of caustic potash. The fatty matters used comprise tallow, palm oil, cocoa-nut oil, lard, oleic acid, castor oil, olive oil, &c. The amount of uncombined alkali in such soaps, although varying greatly, is usually much less than in soft potash soaps. Soaps of this class containing an excess of alkali are used largely for scouring purposes. Others which are neutral or contain an excess of fatty matter are extensively used as "softeners" for treating dyed cotton goods. For this purpose palm oil is the principal fatty matter employed.

Method IV.—Hard soaps made by open-pan boiling, where the glycerin is eliminated by "salting-out," are manufactured on an enormous scale. According to Lant Carpenter, probably 90 per cent. of the total soap produced

in English-speaking countries is made in this way. The principal varieties are known as curd, mottled, and yellow. Almost all kinds of fatty matter are used, and for "yellow household" soaps resin is also largely employed, along with tallow, palm oil, and other fats.

Curd soaps should be free from resin. They are of great importance for milling and scouring dyed fabrics.

Experience shows that, other things being equal, a soda soap exerts a far more marked injurious action on wool than a potash soap; the "suint," or wool grease, of the fleece is a kind of natural soap, and is remarkable in this respect that it scarcely contains any soda, potash being almost the sole alkaline constituent. Accordingly for wool scouring potash soaps free from soda are usually preferred; but, on the other hand, a notable amount of injury to the wool may be brought about if the soap contains any considerable excess of alkali, and more especially if resinate or silicate of potash be also present. A microscopic examination of wool which has been treated with soap shows that the edges of the nests or thimbles (with which a wool fibre may be compared) have been split and appear more or less shrivelled, and the more alkaline the soap the more the fibre was attacked. It is obvious that the more free from surplus uncombined alkali the potash soap is made the more suitable it is for this special purpose; in fact, when the quantity of surplus alkali becomes moderately marked less injury is effected by the use of a soda soap *free from surplus alkali* than by the alkaline potash soap, although a neutral potash soap, of course, produces still less injury. The employment of certain ammonium salts for removing the excess of alkali from soaps depends on the circumstance that potash and soda as also potassium and sodium carbonates possess the property of displacing ammonia from its compounds with acids. For example, ammonium chloride combines with sodium carbonate to form sodium chloride and ammonium carbonate; consequently, if ammonium chloride be added to a soap containing free sodium carbonate, the result is a neutral soap, together with a volatile alkali, which has no injurious effect on wool.

The process of effecting the elimination of surplus alkali may be applied to soft soaps (freed as far as possible from any large excess of alkali by exercising due care in manufacture) by thoroughly crutching in an appropriate amount of the ammoniacal compound before barrelling the soap. All soaps treated in this way emit a smell of ammonia on opening the barrels. Soaps de-alkalised by this method are well suited for use where an article devoid of excess of free alkali is of importance.

Similar remarks apply to "oil" soaps for fulling purposes made from oleic acid, &c., the de-alkalising agent being crutched in as late as possible consistent with due admixture, and the mass allowed to solidify.

For certain purposes, and more particularly for clearing printed calicoes after dyeing with mordants, and similar operations carried out with other cotton goods, an excess of alkali amounting to only 0·1 or 0·2 per cent. is injurious, certain colours being more prone to alteration under such treatment than others; accordingly, the calico printer requires for such purposes a soap as nearly approaching to absolute freedom from excess of alkali as possible. This result is readily attainable by treating the soap before solidifying in the frames with the proper amount of ammoniacal salt, the minute amount of ammonia retained in the bars, after cutting and stacking, exerts a very far less injurious action than the corresponding quantity of fixed alkali upon sensitive colours.

According to Thorp Whitaker,* in many cases, after dyeing, the material (especially wool) contains a considerable amount of free acid, and if a perfectly

* *Journ. Soc. Dyers and Col.*, 1887, p. 41.

neutral soap were used, a portion would be decomposed and free fatty acids deposited on the fibre. In such cases, therefore, a soap containing ¼ per cent. of free alkaline carbonate, if properly used, will not injure the colours, and indeed gives superior results to one absolutely free from excess of alkali.

The following tables show the results of a few analyses made by Rawson of scouring, milling, and softening soaps:—

POTASH SOAPS FOR WASHING RAW WOOL, &c.

In 100 Parts.	Made from Olive and Cotton-seed Oils.	Made from Olive Oil and Tallow.	Made from Olive Oil.	Made from Cotton-seed Oil.	Source unknown.
Water,	42·20	37·10	48 75	41·78	45 95
Combined alkali (K_2O),	9·20	10·08	7·32	9·05	7·78
Fatty anhydride,	43·78	47·50	38·37	43 82	40·36
Potassium hydrate,	·45	·28	·22	·15	1·50 (hydrate and carbonate)
Potassium carbonate,	·82	1·58	2·05	1·40	
Glycerin, &c. (by diff.),	3·55	3·46	3·29	3·80	4·41
Melting point of fatty acids, °C.,	29°	31°	26°	37°	32°

SODA SOAPS.

	For Milling Cloth.			For Scouring Purposes.		
	Made from Tallow.	Made from Tallow and Palm Oil.	Made from Tallow, Cotton-seed Oil, &c.	Made from Palm Oil, Whale Oil, &c.	Made from Olive Oil.	Made from Tallow, Cotton-seed Oil, &c.
Water,	26·73	29·53	23·25	25·38	29·56	18·55
Combined soda (Na_2O),	7·98	7 78	8·57	7·31	7·07	7·98
Sodium carbonate,	·18	·26	·12	·75	·35	·42
Fatty acids,	67·22	64·05	69·50	65·40	64·11	72·60
Melting point of fatty acids, °C.,	44°	40°	38°	36°	23°	37°

"SOFTENING SOAPS" (SODA).

MADE PRINCIPALLY FROM PALM OIL OR PALM OIL WITH OLEIC ACID.

	A.	B.	C.	D.	E.
Water,	66·80	64·40	32·50	28·05	67·50
Combined soda,	3·15	3·40	7·20	7·50	1·05
Fatty anhydrides,	25·95	30·50	54·35	59·15	7·25
Free fat,	1·05	·50	2·20	1·25	22 86
Sodium carbonate,	·15	·10	·25	·20	1·34 (carbonate and glycerin)
Glycerin, &c. (by diff.),	2·90	1·10	3·50	3·85	

Recovery of Fatty Matter from Waste Scouring Liquors.—The waste liquors from the washing of raw wool contain, in addition to the soap and

alkalies which have been used, the "yolk" of the wool. This yolk, which in different classes of wool varies greatly in quantity, is a complicated mixture of fatty and waxy bodies. It contains a considerable proportion of cholesterin and cholesteroid bodies which are unsaponifiable. On the addition of an acid to a solution of soap, the latter is decomposed with the formation of an alkaline salt and free fatty acids which rise to the surface. When sulphuric acid, for example, is added to a solution of potassium oleate (the principal constituent of an olive oil potash soap), free oleic acid rises to the surface, and potassium sulphate remains in solution. The reaction takes place according to the following equation:—

$$2KC_{18}H_{33}O_2 + H_2SO_4 = K_2SO_4 + 2HC_{18}H_{33}O_2.$$

On this principle the recovery of grease or fat from waste scouring liquors depends. The waste liquors are run into large tanks and thoroughly well mixed with a slight excess of sulphuric acid (chamber acid is usually employed for this purpose) by means of long rakes. After standing some hours the crude fatty matter rises to the surface. The under liquid, which contains alkaline sulphates, a little free sulphuric acid and glycerin (if present in the soap used), is run off, and the magma of fatty matter collected and drained on filters made of coarse cocoa-nut matting. The separation of the fatty matter is accelerated by heating the mixture of soapy liquors and sulphuric acid in large wooden cisterns by means of steam, and this method is now generally adopted in modern works. After the excess of liquid has drained away, the magma, which contains in addition to grease much dirt (organic and inorganic), bits of wool fibres, &c., is placed in canvas bags and introduced into a steam press. Steam is slowly admitted, and a gradually increasing pressure applied. The fatty matters melt and flow out of the press along with water into a tank, from which the oil is pumped into a purifying vessel. The cake which is left in the canvas bags still contains from 10 to 15 per cent. of grease, which, in some cases, is extracted by means of carbon disulphide.

The purification of the fatty matter merely consists in boiling it with a small quantity of dilute sulphuric acid. The acid solution is run off, and the oil transferred into casks. On cooling it solidifies into a soft yellowish-brown mass, possessing a somewhat disagreeable odour. It is sold under such names as recovered grease, brown grease, Yorkshire fat, &c.

The composition of this recovered grease varies very greatly according to the kind of wool which has been scoured and the soap used in the operation. Recovered fatty matter from the washing of greasy wool contains a high percentage of wool-fat, much of which is unsaponifiable. If the wool contains but little grease, the recovered fat consists principally of the fatty acids derived from the soap, and contains only a small percentage of unsaponifiable matter. In some cases the wool is steeped in water only previous to scouring, by which means much of the "yolk" and potash salts are removed. When this is done the soapy liquors give a less yield of recovered fat, but it is of superior quality. The following figures show the percentage of saponifiable and unsaponifiable matter in a few samples of recovered grease from wool scouring:—

Unsaponifiable, ...	25·5	35	42·5	8·5	15·6
Saponifiable, ...	74·5	65	57·5	91·5	84·4

When large quantities of alkaline carbonates are used in scouring, the value of the recovered fat may be less than the cost of production. The extent to which waste scouring liquors vary in composition is shown by the following partial analyses. All the four samples were obtained from the washing of raw wool:—

In 100 Parts.	1.	2.	3.	4.
Water, ...	99·38	97·10	96·50	97·80
Mineral matter, ...	·15	1·05	1·30	·60
Oil or grease, ...	·27	1·20	1·52	1·36
Other organic matter (by diff.), . .	·20	·65	·68	·24
	100·00	100·00	100·00	100·00
Lbs. of pure sulphuric acid required to neutralise 1,000 gallons, ...	7	14	44	22
Lbs. of recovered fat per 1,000 gallons, .	27	120	152	136

After wool has been washed it is treated with a certain amount of oil (usually Gallipoli olive oil) to facilitate the carding operation. The wool, in the form of sliver, is subsequently washed with soap in what is known as a back-washing machine. In most works the waste "suds" from this operation are mixed with the waste liquors obtained in washing the raw wool. It is far preferable, however, to treat the waste liquor from the back-washing machines separately, since the recovered fatty matter, containing but very little unsaponifiable matter is much more valuable than the common brown grease.

The waste liquors from yarn scouring (especially worsted yarn) also yield a superior quality of recovered fat, consisting, as a rule, only of the fatty acids derived from the soap and vegetable oils.

Ammonia, NH_3—Ammonium Hydroxide, NH_4OH—*Liquor Ammoniæ.*—Ammonia is obtained by heating ammonium sulphate with lime—

$$(NH_4)_2SO_4 + Ca(OH)_2 = 2NH_3 + CaSO_4 + 2H_2O.$$

The solution is obtained by distillation of ammonia liquor from gas works.

Ammonia (NH_3) is a colourless gas of a most pungent and peculiar smell, by means of which it can be readily recognised. It is exceedingly soluble in water, 1 volume of water dissolving, at 15° C., 730 volumes of ammonia; it is also very soluble in alcohol. The gas is driven out of both liquids by heat, and in open vessels it slowly escapes into the surrounding atmosphere. Ammonia can easily be liquefied by pressure, and the liquid is sold in a nearly pure state in iron cylinders under the name of "anhydrous ammonia." When liquefied ammonia evaporates under reduced pressure, it absorbs heat, and is, on this account, largely used in the manufacture of artificial ice.

The colourless liquid known under the name of *ammonia* is a solution of ammonia gas in water, and is supposed to contain the hydroxide NH_4OH. The liquor has a specific gravity of about 0·88—*i.e.*, it is lighter than water, and the solution is lighter the more ammonia it contains. (See table, p. 215.)

Ammonia, both in the gaseous state and in solution, evinces very strong basic properties; it turns red litmus blue, and neutralises even the strongest acids, forming salts with them, which show a remarkable resemblance to the salts of potassium and sodium. The salts of ammonium contain the monovalent radical ammonium, NH_4; and the corresponding hydroxide, $NH_4(OH)$, probably exists in the solution of the gas—$NH_3 + H_2O = NH_4(OH)$. Many salts of ammonia dissociate into the component acid and gaseous

SPECIFIC GRAVITY OF LIQUOR OF AMMONIA AT 15° C. (*Lunge and Wiernik*).

Specific Gravity at 15°.	Per cent. NH_3.	1 Litre contains grms. NH_3.*	Correction of the Specific Gravity for ± 1° C.	Specific Gravity at 15°.	Per cent. NH_3.	1 Litre contains grms. NH_3.	Correction of the Specific Gravity for ± 1° C	Specific Gravity at 15°.	Per cent. NH_3.	1 Litre contains grms. NH_3	Correction of the Specific Gravity for ± 1° C.
1·000	0·00	0·0	0·00018	0·960	9·91	95·1	0·00029	0·920	21·75	200·1	0·00047
0·998	0·45	4·5	0·00018	0·958	10·47	100·3	0·00030	0·918	22·39	205·6	0·00048
0·996	0·91	9·1	0·00019	0·956	11·03	105·4	0·00031	0·916	23·03	210·9	0·00049
0·994	1·37	13·6	0·00019	0·954	11·60	110·7	0·00032	0·914	23·68	216·3	0·00050
0·992	1·84	18·2	0·00020	0·952	12·17	115·9	0·00033	0·912	24·33	221·9	0·00051
0·990	2·31	22·9	0·00020	0·950	12·74	121·0	0·00034	0·910	24·99	227·4	0·00052
0·988	2·80	27·7	0·00021	0·948	13·31	126·2	0·00035	0·908	25·65	232·9	0·00053
0·986	3·30	32·5	0·00021	0·946	13·88	131·3	0·00036	0·906	26·31	238·3	0·00054
0·984	3·80	37·4	0·00022	0·944	14·46	136·5	0·00037	0·904	26·98	243·9	0·00055
0·982	4·30	42·2	0·00022	0·942	15·04	141·7	0·00038	0·902	27·65	249·4	0·00056
0·980	4·80	47·0	0·00023	0·940	15·63	146·9	0·00039	0·900	28·33	255·0	0·00057
0·978	5·30	51·8	0·00023	0·938	16·22	152·1	0·00040	0·898	29·01	260·5	0·00058
0·976	5·80	56·6	0·00024	0·936	16·82	157·4	0·00041	0·896	29·69	266·0	0·00059
0·974	6·30	61·4	0·00024	0·934	17·42	162·7	0·00041	0·894	30·37	271·5	0·00060
0·972	6·80	66·1	0·00025	0·932	18·03	168·1	0·00042	0·892	31·05	277·0	0·00060
0·970	7·31	70·9	0·00025	0·930	18·64	173·4	0·00042	0·890	31·75	282·6	0·00061
0·968	7·82	75·7	0·00026	0·928	19·25	178·6	0·00043	0·888	32·50	288·6	0·00062
0·966	8·33	80·5	0·00026	0·926	19·87	184·2	0·00044	0·886	33·25	294·6	0·00063
0·964	8·84	85·2	0·00027	0·924	20·49	189·3	0·00045	0·884	34·10	301·4	0·00064
0·962	9·35	89·9	0·00028	0·922	21·12	194·7	0·00046	0·882	34·95	308·3	0·00065

* The number of pounds of NH_3 per gallon is found by dividing by 100 the number in the third column (grammes of NH_3 per litre).

ammonia when strongly heated — $NH_4Cl = NH_3 + HCl$; and when their solutions are heated with soluble bases, ammonia is driven off, while the base combines with the acid—

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

The same reaction takes place between the dry substances (see above).

Ammonia is always present in the atmosphere in minute quantities, being produced by electricity, by the evaporation of water into the air, by the decomposition of vegetable and animal nitrogenous matter, and by many other processes. Hence the air has a slightly alkaline reaction, except in localities where much coal is burnt, when it usually acquires an acid reaction, especially when the fuel used contains much sulphur. While the atmosphere of the great cities is usually acid from sulphuric and sulphurous acids, the country air is frequently alkaline.

Ammonia is employed for the purpose of neutralising acids in many industries (ammonia-soda, dyestuffs, &c.). By dyers it is used when a milder alkali than caustic soda is wanted; or where its volatility allows of the ready removal of an excess of the alkali, as, for instance, in neutralising Turkey-red oil. It is also used as a fixing agent for some metallic mordants—*e.g.*, lead salts and basic iron salts.

Ammonium Sulphate, $(NH_4)_2SO_4$, is the principal commercial salt of ammonia, and is obtained as a bye-product in gas and coke works; also in the blast furnace and in the Mond gas process. It is used as a constituent of the so-called metachrome mordant (see *Chromium*), and for the manufacture of ammonia and its salts.

Ammonium Chloride, NH_4Cl—*Sal Ammoniac.*—This salt occurs as a tough fibrous mass, or crystallises in arborescent forms of the regular system. It is very soluble in water, and, when heated, it volatilises completely without melting. Ammonium chloride is used for the fixation of aluminate of soda on the cotton fibre, in aniline black dyeing, &c.

Ammonium Carbonate, $(NH_4)_2HCO_3$—*Sal volatile; Salt of Hartshorn.*—The so-called *salt of hartshorn* only is of practical importance. It consists of *ammonium bicarbonate*, $(NH_4)HCO_3$, and *ammonium carbamate*, $CO(NH_2)(ONH_4)$, the salt of *carbamic acid*, $CO(NH_2)(OH)$. It is formed by the putrefaction of nitrogenous substances like urine. In former times it was obtained by the destructive distillation of hide clippings, bones, or horn; hence the name salt of hartshorn (and spirit of hartshorn for ammonia-water). At present it is produced by heating ammonium sulphate with chalk. It forms a white semi-transparent fibrous mass which is readily soluble in water, smells of ammonia, and absorbs from the atmosphere moisture and carbonic acid, forming **ammonium bicarbonate.** When the salt is dissolved in water the ammonium carbamate is changed into the *normal ammonium carbonate*, $(NH_4)_2CO_3$, which is also known in the free state.

Commercial ammonium carbonate or salt of hartshorn is used as a fixing agent for aluminium mordants in place of urine.

Urine is secreted by the kidneys from the arterial blood; it contains in solution a part of the nitrogenous waste of the animal organism in the form of *urea*, $CO(NH_2)_2$, and *uric acid* ($C_5H_4N_4O_3$). By putrefaction or fermentation the urea is converted into ammonium carbonate (as indicated by the smell of putrid urine)—$CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3$.

The action of urine is chiefly due to this ammonium carbonate, which has a mild alkaline character. However, the fatty and albuminous substances, together with the small amount of ammonium phosphate found in urine, may exert some influence. At present urine is used to a small extent only, because substitutes have been found which are more regular in composition

and pleasanter to work with, especially ammonia and carbonate of ammonium. The human urine only is used. It is employed in washing wool, in preparing some colouring matters, as orchil and cudbear, in the preparation of indigo-vats, and as a fixing agent of aluminium mordants.

Cow-dung.—Under this name are generally comprised the various kinds of dung, such as sheep's dung, &c. Dung contains a mixture of phosphates, carbonates, silicates, sulphates, and chlorides of calcium, potassium, sodium and ammonium, and other salts, albuminoïd compounds, fatty acids, fibrous matter, and various other substances. When fresh it never has an acid reaction, and rarely a basic one. It is principally employed in so fixing the mordants on cotton piece goods prior to these being dyed, that the white parts shall remain clear. The action of cow-dung has not been completely explained; the phosphates, silicates, and carbonates doubtless exert a fixing action, but the organic substances are not altogether inert. It is known that the latter are capable of forming precipitates with metallic oxides—*e.g.*, with red liquor—while they also act mechanically by absorbing the loosely adhering mordants and removing them completely from the fibre, so as to prevent them from spoiling the white of printed goods. It is asserted that cow-dung gives better results than any substitute, such as the arsenates, phosphates, silicates, or carbonates; while it seems to act more slowly and evenly. The dunging bath is principally made up with cow- or sheep-dung, and should not contain too much straw or iron; before being used it is often allowed to stand for some days with addition of some caustic soda, and subsequently diluted with 50 to 60 times its volume of water; the temperature of the dunging bath should be 50° to 65°.

Ammonium Acetate, $(NH_4)C_2H_3O_2$, forms crystals which are exceedingly soluble in water, but not deliquescent in the air. The dry salt is decomposed when heated. The salt is also used as an addition to the dye-bath in the dyeing of woollen goods or glorias (wool-silk) with Alizarins and acid or direct cotton colours, in order to effect an even and thorough dyeing of the goods. Its action is based on its alkaline reaction, which, however, becomes acid on boiling in consequence of the evolution of ammonia. Thus it prevents, at first, the dyestuffs from being too rapidly fixed, but gradually it assists an even fixation by causing the bath to become acid.

Ammonium acetate, on account of its mild alkalinity, which does not affect the fibre, is also used for stripping colours from wool and silk.

It may easily be prepared by mixing equivalent quantities of acetic acid and ammonia. The aqueous solution is found in commerce.

Ammonium Sulphocyanide or Thiocyanate, $(NH_4)CNS$, crystallises in colourless laminæ. It is very soluble in water and in alcohol, and absorbs heat on dissolving. The solution of the salt smells of ammonia, and has an alkaline reaction. It may be used for neutralising acids, which, by dissolving iron, are liable to transfer it to the colour. In order to prevent the action of copper on certain dyestuffs it is also added to the dye liquor, an insoluble coating of cuprous sulphocyanide being formed on the copper. Very minute quantities of the salt are sufficient.

Ammonium Oxalate, $(NH_4)_2C_2O_4 + H_2O$, forms rhombic crystals, of which one part dissolves in 23 parts of water at 15°. This salt is sometimes used in wool dyeing to correct the hardness of the water and thus to prevent the precipitation of the dyestuffs by lime salts.

Calcium Oxide, CaO—*Quicklime; Burnt Lime.*—Calcium oxide is prepared by subjecting calcium carbonate (marble, limestone, oyster shells, &c.), to a bright red heat, $CaCO_3 = CaO + CO_2$. The purest product is obtained from marble. Calcium oxide is a white, amorphous, porous mass of 3·08 specific

gravity, which cannot be melted. It attracts moisture with great avidity, and with evolution of heat. It also absorbs carbonic acid from the air.

Calcium Hydroxide, $Ca(OH)_2$—*Calcium Hydrate; Slaked Lime.*—Calcium hydroxide is formed by the action of water on calcium oxide, $CaO + H_2O = CaO_2H_2$; or, as it is commonly called, "slaking" of lime, which is best effected by first moistening the quicklime with small quantities of hot water until the mass becomes very hot and begins to break up, and then adding more cold water. If the raw material contained clay, and has been heated too strongly, the quicklime does not slake well, and yields no good caustic lime. Calcium hydroxide forms a white powder of 2·01 specific gravity, which dissolves in 730 parts of water at 15°, and is less soluble at higher temperatures. The solution is called *lime water.*

Water containing calcium bicarbonate or organic substances is not well suited for making lime water, as the lime will soon be covered with insoluble substances, and be dissolved but slowly by the water. Lime water containing undissolved slaked lime, so as to appear milky, is known as *milk of lime.*

Dry calcium hydrate has recently been placed on the market by The Water-Softening Materials Co., of Greenwich, and is sold in bags. It is claimed by the makers to be perfectly stable in the air, and to be specially suited for all chemical operations on account of its constant composition.

Calcium hydroxide is decomposed at a red heat into calcium oxide and water. It is a strong diacid base, turns red litmus blue, and absorbs with avidity carbon dioxide from the air, forming insoluble calcium carbonate, and rendering the liquid turbid. Calcium hydroxide is precipitated from the aqueous solution of calcium salts, if they are not too dilute, by caustic potash or caustic soda; in no case by ammonia. Hence strong solutions of potassium or sodium carbonate cannot be causticised with lime, but must be diluted to a specific gravity of 1·08 to 1·10 (16° to 20° Tw.). In various chemical industries calcium hydrate is an important material—*e.g.*, in the manufacture of chloride of lime, caustic soda, &c. By bleachers and dyers it is used as a cheap alkali for bleaching cotton, as a fixing agent of iron mordants, in the preparation of the indigo-vat, &c. When solid (*i.e.*, lumpy) lime has been long in contact with cotton, it is liable to tender the fibre, and to cause uneven dyeing.

Calcium Sulphate, $CaSO_4$.—Calcium sulphate can hardly be said to belong to the class of dyers' materials; but it is certainly a very important substance in dyeing, because it is usually present in water, and is the chief substance which gives rise to the *permanent hardness of water.* It occurs crystallised in nature as anhydrite, $CaSO_4$, and, combined with water, as gypsum and alabaster, $CaSO_4 + 2H_2O$. Calcium sulphate is soluble in about 400 parts of cold water and is less soluble in hot water. Gypsum when moderately heated loses its water, forming the so-called plaster of Paris. This takes up 2 molecules of water again when moistened, and forms a solid mass. Artificially prepared calcium sulphate or "annaline" is used by paper manufacturers.

Calcium Chloride, $CaCl_2$, is formed by the action of hydrochloric acid on lime or chalk; and is obtained as a bye-product in many chemical processes—*e.g.*, in the manufacture of ammonia-soda.

Calcium chloride is an extremely soluble and deliquescent substance, which is found in commerce as a white porous or as a solid dense mass; it also forms crystals with 6 equivalents of water. 100 parts of water dissolve 63 parts of calcium chloride at 10° C., 120 at 40° C.; and 139 at 60° C.

Calcium Hypochlorite, $Ca\begin{Bmatrix} Cl \\ OCl \end{Bmatrix}$ or $Ca(OCl)_2 + CaCl_2$ (?)—*Chloride of Lime* or *Bleaching Powder.*—Chloride of lime is produced by the action of chlorine gas on lime. The chlorine is passed over calcium hydroxide, which

is spread in thin layers in lead chambers. Both the exact composition of the product and the chemistry of the process by which it is generated are still more or less obscure. The commercial product contains 35 to 39 per cent. available chlorine—*i.e.*, available in the form of hypochlorous acid. By the action of chlorine on calcium hydrate, calcium hypochlorite, $Ca(OCl)_2$, is formed according to the equation—$2Ca(OH)_2 + 2Cl_2 = Ca(OCl)_2 + CaCl_2 + 2H_2O$.

Chloride of lime is considered to be a similar compound. Bleaching powder, the commercial article, is a soft white powder which should not contain any lumps. It has the smell of hypochlorous acid and slowly becomes moist in the air. It is soluble in twenty times its own weight of water, but always leaves some insoluble residue. The solution on being heated gives off oxygen, while calcium chloride and calcium chlorate are formed. A solution containing an excess of caustic alkali is not readily decomposed by boiling. Carbonic acid expels the hypochlorous acid; and in this way chloride of lime is decomposed by the atmosphere—$2CaOCl_2 + H_2CO_3 = CaCO_3 + CaCl_2 + 2HOCl$. Hypochlorous acid subsequently decomposes, forming oxygen in the nascent state—$HClO = HCl + O$.

To the oxidising action of this oxygen is due the bleaching power of chloride of lime and of all hypochlorites (*Eau de Javelle*, &c.). The effect of all these compounds is increased if some acid is added to the solution of bleaching powder; only a very small amount of acid is required to start the reaction, fresh acid being generated by the process itself, so that it becomes continuous. $Ca(OCl)_2 + 2HCl = CaCl_2 + 2HOCl$; $2HOCl = 2HCl + 2O$. The employment of formic and acetic acid, for this purpose, has been recommended by G. Lunge.

Chloride of lime, when used for the bleaching of cotton and linen goods, is applied in the form of a perfectly clear very diluted solution, 1·003 to 1·007 specific gravity ($\frac{1}{2}°$ to $1\frac{1}{2}°$ Tw.). If solid lumps of chloride of lime should occur in the solution they may settle on the fibre, so as to weaken it, or at least may give rise to uneven dyeing by forming oxycellulose. The solution should be prepared in the cold because chloride of lime is decomposed on boiling (see above).

The largest quantities of bleaching powder are consumed for the bleaching of cotton, flax, hemp, and materials for the manufacture of paper; while next in importance is its use as a disinfectant. It is also used largely as an oxidising agent in various chemical industries—*e.g.*, as a discharging agent in calico printing.

The preparation of solutions of bleaching powder is not a very simple nor an economical operation. Where the expense of carriage is not too great the liquor (bleaching liquor), made direct from milk of lime, is bought from the works by the consumers.

Other bleaching liquors, the active constituents of which are hypochlorites, are also used. The most important of these is sodium hypochlorite. In addition may be mentioned the hypochlorites of magnesium, of zinc, and of aluminium; the last named is known as Wilson's bleaching liquor.

Calcium Carbonate, $CaCO_3$—*Chalk, Carbonate of Lime.*—Calcium carbonate occurs widely diffused as chalk, limestone, coral, marble, calc-spar, and aragonite—in the amorphous and in various crystallised forms. It is almost insoluble in water (2 parts in 100,000 parts of cold or boiling water); but more soluble in water containing carbonic acid (88 parts in 10,000 parts of such water at 10°). When the carbonic acid is driven from the water by heat, the calcium carbonate is precipitated. The hardness of natural waters, due to dissolved calcium bicarbonate, is known on this account as *temporary hardness.* Calcium carbonate has mild basic properties, and is readily decomposed by acids. It is used by chemical manufacturers to neutralise acid

liquids, and by dyers as a mild alkali for neutralising acids for the fixing of mordants (Turkey-red dyeing, "chalking"), and for introducing into the dye-bath the amount of lime necessary for the dyeing with Alizarin. For these purposes it should be light, soft, and almost completely soluble in diluted hydrochloric or acetic acid. It should not contain carbonates or hydroxides of the alkalies. The latter can be detected by the reaction of an aqueous extract on phenolphthalein, which must not be coloured thereby.

Calcium Sulphocyanide or Thiocyanate, $Ca(CNS)_2$, crystallises with 3 equivalents of water, and is very soluble in water. The crude liquor, obtained from gas water, is used for the preparation of other sulphocyanides in textile printing.

Calcium Acetate, $Ca(C_2H_3O_2)_2$—*Acetate of Lime.*—Calcium acetate is produced by neutralising acetic acid with lime. It crystallises with 1 equivalent of water, $Ca(C_2H_3O_2)_2 + H_2O$. It is very soluble in water, is precipitated from solution by alcohol, and, chemically, acts as a neutral salt, although it turns red litmus blue.

Calcium acetate occurs in two forms in commerce—*brown* or *grey acetate of lime*, the crude product obtained from pyroligneous acid; and *white acetate of lime*, a purer article. To obtain pure calcium acetate, free from iron, dyers prepare it for themselves by neutralising lime with acetic acid—about 7 parts of acetic acid (30 per cent. strength) to 1 of quicklime (CaO) are necessary; litmus paper does not show the point of neutralisation, but phenolphthalein paper may be used for this purpose.

Calcium acetate is a mordant proper, since calcium is an integral constituent of the Alizarin lakes, and it is introduced into the colour in the form of the acetate; it is also used in the preparation of other acetates which serve as mordants—*e.g.*, aluminium acetate; but its principal use is in the manufacture of acetic acid.

Barium Peroxide, BaO_2.—Barium peroxide is produced when a current of oxygen is passed over gently-heated barium oxide. It forms a greyish-white porous mass, and dissolves in dilute acids, forming peroxide of hydrogen—

$$BaO_2 + 2HCl = H_2O_2 + BaCl_2.$$

On the other hand, barium salts in alkaline solutions are converted by hydrogen peroxide into barium peroxide—

$$BaCl_2 + H_2O_2 + Ba(OH)_2 = BaO_2 + BaCl_2 + 2H_2O.$$

On being heated beyond 400° C., barium peroxide is decomposed into oxygen and barium oxide. Barium peroxide is used for the preparation of hydrogen peroxide, and of pure oxygen.

Barium Sulphocyanide or Thiocyanate, $Ba(CNS)_2$, crystallises with 2 molecules of water, and is very soluble and deliquescent. It is used for the preparation of sulphocyanides, which serve as mordants in textile printing. The commercial article contains barium chloride as an impurity.

Magnesium, Mg, is a silver-white metal which does not rapidly oxidise in the air. It burns with a dazzling white light, which is extremely rich in chemically active rays. It forms a valuable substitute for sunlight in photography, and is used by dyers for matching-off colours when daylight is not available.

Magnesium Oxide or *Magnesia usta*, MgO, and **Magnesium Hydroxide,** $Mg(OH)_2$, are white amorphous powders, almost insoluble in water. They are weak binacid bases, and are readily soluble in most acids. With the fatty acids they form insoluble soaps.

Magnesium Sulphate, $MgSO_4$, occurs in nature as *kieserite*, $MgSO_4 + H_2O$, and as *Epsom salt*, $MgSO_4 + 7H_2O$. The former is almost insoluble in water; the latter is very soluble in water (1 in 3 parts at 15° C.). It is prepared on the large scale from kieserite and magnesite, and occurs in commerce in rhombic crystals or as a crystalline powder. Magnesium sulphate is used in medicine, in wool dyeing (for some basic colours), and in enormous quantities for the finishing of cotton goods. If used for the latter purpose, it should not contain any magnesium chloride, as the latter is liable to generate hydrochloric acid in the free state at the temperature of the callender roller, and thus might tender the fibre.

Magnesium Chloride, $MgCl_2$, is a very soluble and deliquescent substance and is extensively used as an addition to size for cotton warps. On being heated it decomposes into *magnesium oxychloride*, $MgCl(OH)$, and hydrochloric acid. As mentioned above, it is liable to weaken the fibre under certain conditions. Water containing much magnesium chloride is not suitable for feeding steam boilers, because the acid which is set free corrodes the iron.

Magnesium Carbonate, $MgCO_3$, is found native as magnesite. It is almost insoluble in pure water, but readily soluble in water containing ammonium salts or carbonic acid.

Magnesium Acetate, $Mg(C_2H_3O_2)_2$, crystallises with 4 equivalents of water. It is very soluble. It has been proposed as a mordant (compound mordants, H. Koechlin), and can be obtained by the double decomposition of magnesium sulphate and lead acetate, or by dissolving magnesium carbonate in acetic acid. In printing colours for calico, it plays the part of a powerful alkali.

ALUMINIUM, Al = 27·1.

In the pure state, aluminium is a perfectly white metal, but as produced it has a bluish-white tinge; the specific gravity is 2·5, the melting point about 700° C. Under all ordinary conditions it is not acted upon by air and moisture, sulphuretted hydrogen, ammonium sulphide, or cold acids, except hydrochloric acid. The non-corrodibility, however, depends upon the freedom of the metal from silicon, iron, and the commercial product is more or less easily attacked by chemical agents. Aluminium is readily corroded by alkaline solutions which form aluminates, by hydrochloric acid and chlorine, and is acted upon more or less by solutions of chlorides. Salts of aluminium are not poisonous.

Aluminium is a trivalent metal. The formulæ of aluminium compounds are usually written with 2 atoms of aluminium, like $Al_2(OH)_6$ instead of $Al(OH)_3$, and Al_2Cl_6 instead of $AlCl_3$, because aluminium was supposed to be quadrivalent, and to play the part of a hexad in the combination of 2 atoms, like $\equiv Al—Al \equiv$ or Al_2^{vi}.

Aluminium Oxide, Al_2O_3—*Alumina.*—Aluminium oxide occurs native as corundum, ruby, sapphire, and emery. It is prepared as an amorphous powder of 3·75 to 3·9 specific gravity by heating aluminium hydroxide. When prepared by gentle heat it is readily soluble in acids; by the application of higher temperatures, however, it becomes insoluble in acids. All modifications of alumina become soluble in acids, when melted with caustic alkalies.

Aluminium Hydroxides, Aluminium Hydrate, Alumina.—The *Aluminium hydroxide*, $Al(OH)_3$ or $Al_2(OH)_6$, is formed when ammonia is added to the solution of an aluminium salt—$Al_2(SO_4)_3 + 6NH_3 + 6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4$; when precipitated from boiling solutions it is very difficult to dissolve in weak acids—*e.g.*, sulphurous or acetic acid: from cold solutions it is obtained as a gelatinous substance, from hot solutions as a white powder; the presence of organic substances like oxalic, tartaric, or citric acid or

sugar may prevent the precipitation more or less. The dry mass on being heated is converted into the *aluminium hydroxide*, $AlO(OH)$ or $Al_2O_2(OH)_2$, and by continued heating into the oxide, Al_2O_3. *Aluminium hydroxide*, $Al_2O(OH)_4$, which is, like the preceding compounds, not soluble in water, is obtained by boiling the ordinary hydroxide, $Al(OH)_3$, with water for 24 hours. According to E. Schlumberger,* it is, however, not possible to obtain the normal hydroxide, the products always containing acid or less hydroxyl-groups than demanded by the formula $Al(OH)_3$. Graham obtained by dialysis of aluminium hydroxide, which was dissolved in a solution of aluminium chloride, a *soluble hydroxide*, $Al(OH)_3$. This substance coagulates on heating, as also on the addition of acids, bases, and salts; it is attracted by the textile fibres, and acts as a mordant. Schlumberger states, however, that colloidal aluminium hydroxide does not act as a mordant. Another *soluble hydroxide*, $Al_2O(OH)_4$, was prepared by Walter Crum † by heating a solution of aluminium acetate, which contained 1 part of aluminium, in 200 parts of water, for 24 hours in a closed vessel. This compound coagulates like Graham's hydroxide, but does not behave as a mordant.

Aluminium hydroxide acts both as a weak (triacid) base and as a very weak acid. It forms *aluminium salts* with acids, and *aluminates* with bases.

Aluminium hydroxide is also precipitated from the solutions of the aluminium salts by the hydroxides and carbonates of potassium and sodium; organic substances prevent the precipitation more or less. According to Schlumberger, the precipitates of aluminium salts produced by carbonates always contain some carbonic acid, and he succeeded in preparing the basic carbonate, $Al_4(OH)_{10}CO_3$, H_2O. By an excess of caustic potash or soda the hydroxide is readily redissolved (with formation of the aluminates); ammonium salts, especially on boiling, prevent it to a great extent from redissolving. The hydroxide does not dissolve in ammonia unless a great excess of caustic ammonia is applied, and when no considerable quantities of ammonium salts are present. An excess of the carbonates dissolves but very little of the hydroxide.

Caustic alkalies do not redissolve aluminium hydroxide if the precipitation has been effected in the presence of a magnesium salt (*Double Mordants* of Horace Koechlin). In mordanting with the acetates of alumina or chrome, acetate of magnesium (or calcium) is added to the dye-bath for fixing on cotton such colours as Phloxin or Xylidine-scarlet. A method indicated by Koechlin for the dyeing of St. Denis red consists in working the fibre in a mixture of aluminium and magnesium salt, and then passing it through a solution of zincate of soda. The substitution of the latter for caustic soda, introduced by C. Weber of Winterthur, has the advantage of fixing an insoluble aluminate of zinc in the fibre; in this particular case a *triple mordant* is formed.‡

Aluminium hydroxide, on being precipitated from solutions of aluminium salts, attracts many inorganic and organic substances which are in the same liquid, either in suspension or in solution, and is used on this account in clarifying drinking water, sugar solutions, &c. Many vegetable and artificial colouring matters are also attracted by aluminium hydroxide and precipitated from their solutions, forming "colour-lakes"; the liquid thereby becomes decolourised if enough aluminium hydroxide is used. The lake-forming action of the aluminium mordants when fixed on the fibre is precisely similar.

Aluminates.—Aluminium hydroxide possesses the character of a weak acid, and forms with basic hydroxides salts which are called aluminates.

The aluminates are prepared by melting aluminium oxide with bases or with the corresponding carbonates. Potassium and sodium aluminates are

* *Journ. Soc. Dyers and Col.*, 1895, p. 105. † *Liebig's Ann.*, 89, p. 168.
‡ Prudhomme, *Journ. Soc. Dyers and Col.*, 1891, p. 133.

also obtained by dissolving aluminium hydroxide in caustic potash and caustic soda. The aluminates which are produced in the dry way are derivatives of the aluminium hydroxide, AlO_2H—*e.g.*, $Ba(AlO_2)_2$. A great many of these occur as minerals. Potassium aluminate is obtained in crystals from aqueous solutions, as $Al(OH)_2(OK)$, or $2Al(OH)_2OK + H_2O$. Sodium aluminate has not been prepared in a crystalline form.

On the whole the acid character of aluminium hydroxide is less distinct than the basic. The solutions of aluminates are decomposed by all acids, even by carbonic acid; aluminium hydroxide is precipitated and a potassium or sodium salt remains in solution. In a similar way the solutions of aluminates are decomposed by ammonium salts; potash or soda, as the stronger bases, combine with the acid of the ammonium salt, whereas the liberated aluminium hydroxide does not combine with the ammonia and remains in the free state in the form of a gelatinous precipitate—$Al(OH)_2OK + NH_4Cl = Al(OH)_3 + KCl + NH_3$. Use is made of this reaction in fixing the mordant.

Aluminate of Soda—*Alkaline Pink Mordant.*—This article is prepared by heating cryolite with lime or bauxite with soda ash. It can also be obtained by adding caustic soda to a strong solution of aluminium sulphate until the precipitate at first formed is redissolved, and no fresh precipitate is produced on addition of more caustic lye. A slight excess of alkali makes the solution more stable and is not injurious. If a small amount of caustic lye is used the precipitate redissolves also at first with formation of basic aluminium sulphate; on adding more alkali, however, a fresh precipitate is formed, until all sulphuric acid is neutralised by the caustic soda. Aluminate of soda occurs in commerce as a lumpy powder of a white, slightly greenish colour. It is readily soluble in water, but not deliquescent, and is decomposed by carbon dioxide in the presence of moisture. It is used as a mordant for Alizarin red on cotton piece goods (see *Schlieper's process*), but cannot well be employed on cotton yarn on account of the caustic action it has on the hands of the workmen.

Aluminate of soda offers the great advantage that it does not carry iron into the ultimate colour, and that it is fixed on the fibre in a short time without ageing. It finds but limited employment, because it cannot be associated with acid mordants. The goods are simply impregnated with the aluminate, rapidly dried at an elevated temperature, and passed through a solution of ammonium chloride (10° Tw.) at 50° to 60° C. The aluminium is thus fixed in the form of aluminium hydroxide. The hydroxide is also fixed to some extent by mere exposure to the atmosphere. Other salts can be substituted for the ammonium chloride—*e.g.*, zinc sulphate, chloride, or acetate. It seems, however, that they do not offer any advantages over the ammonium salts. Aluminate of soda is not used as a mordant for wool or silk, because it is too alkaline for these fibres.

Aluminium Salts.—The salts which aluminium forms with acids are colourless. Most of the ordinary salts are readily soluble in water, and possess a sweet astringent taste, redden blue litmus, and lose their acid if subjected to strong heat. The solutions of the normal aluminium salts are not decomposed by boiling or by dilution with water (in contrast with the basic salts). They are not changed by carbon dioxide or by sulphuretted hydrogen, neither a carbonate nor a sulphide being formed. On addition of ammonium sulphide no sulphide is obtained; the sulphuretted hydrogen is simply liberated, and aluminium hydroxide formed—

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4 + 3H_2S.$$

The behaviour towards alkalies, &c., has been described with the hydroxide.

Sodium phosphate precipitates from the solutions of aluminium salts,

aluminium phosphate, $AlPO_4$. $Al_2(SO_4)_3 + 2Na_2HPO_4 = 2AlPO_4 + Na_2SO_4 + 2NaHSO_4$. The precipitate forms a voluminous white mass, which is soluble in caustic soda, but not in ammonia. It also dissolves in hydrochloric or nitric acid, but not in acetic acid. Citric acid prevents the formation of the precipitate, but not tartaric acid or sugar. Aluminium phosphate is soluble in the aqueous solutions of other aluminium salts. One equivalent of aluminium sulphate, $Al_2(SO_4)_3$, can keep one equivalent of aluminium phosphate, $AlPO_4$, in solution, according to Liechti and Suida.* This is probably the reason why sodium phosphate is not a good fixing agent for aluminium mordants.

Sodium arsenate precipitates from the solutions of aluminium salts *aluminium arsenate* as a white powder, which is insoluble in water, but soluble in acids. This reaction is used to fix aluminium mordants on the vegetable fibres.

Sodium silicate precipitates from the solutions of aluminium salts aluminium hydroxide; the silicic acid does not combine under these conditions with alumina; if the silicate of soda contains an excess of caustic soda, the precipitate of aluminium hydroxide may redissolve in the precipitant.

Basic Aluminium Salts.—Aluminium salts dissolve freshly-precipitated aluminium hydroxide, forming basic salts, as exemplified in the following equation:—

$$Al_2(SO_4)_3 + Al(OH)_3 = 3Al(SO_4)(OH).$$

Basic salts are also obtained in a soluble form by adding the requisite amount of the hydroxides or carbonates of potassium, sodium, ammonium, or calcium to the solutions of the normal salts, as shown by the following equations:—

$$Al_2(SO_4)_3 + 2NH_3 + 2H_2O = 2Al(SO_4)(OH) + (NH_4)_2SO_4.$$
$$2Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = Al_4(SO_4)_3(OH)_6 + 3Na_2SO_4 + 3CO_2.$$
$$Al_2(SO_4)_3 + 2CaCO_3 + 2H_2O = Al_2(SO_4)(OH)_4 + 2CaSO_4 + 2CO_2.$$

The solutions of the basic salts are more or less rapidly dissociated into normal salts and hydroxide, which latter is precipitated. For instance— $3Al_2(SO_4)(OH)_4 = Al_2(SO_4)_3 + 4Al(OH)_3$. The dissociation is effected by heating or by dilution with water, and takes place the more readily the greater the basicity of the salt is. The presence of other sulphates—*e.g.*, sodium sulphate—in solution causes the basic salts to dissociate more readily. According to Henri Schmid,† however, dissociation is delayed by sodium sulphate, and in its presence basic salts may remain in solution which otherwise would be precipitated.

Probably still more basic sulphates than the compound, $Al_2SO_4(OH)_4$, exist. These, however, are insoluble in water.

Aluminium Sulphate, $Al_2(SO_4)_3 + 18H_2O$.—Aluminium sulphate is prepared by dissolving aluminium oxide or hydroxide in sulphuric acid. On the large scale, aluminium hydroxide (obtained from cryolite, $AlNa_3F_6$), or clay (aluminium silicate), or bauxite (alumina containing ferric oxide) is dissolved in sulphuric acid, and the mass is evaporated until it solidifies on cooling.

Aluminium sulphate in the pure state forms monoclinic tablets which contain 18 molecules water of crystallisation and dissolve very easily in water. In alcohol it is insoluble. The commercial article, known under the names of *cake alum*, *patent alum*, and *concentrated alum*, occurs as a solid mass or irregular lumps, having a fused appearance. It often contains more than 55 per cent. $Al_2(SO_4)_3$, and should not contain less than 48 per cent.; the pure salt, $Al_2(SO_4)_3 + 18H_2O$, contains 51·35 per cent. $Al_2(SO_4)_3$. The article must be free from iron and from an excess of acid; the former injures the ultimate

* *Journ. Soc. Chem. Ind.*, 1883, p. 537. † *Chemiker Zeitung*, 1895, p. 777.

shade, while the latter is liable to weaken the vegetable fibres and to affect the reactions. It is not easy for the manufacturer to satisfy these demands; excellent qualities, however, are now produced; still aluminium sulphate should be carefully examined before use for free acid, iron, and percentage of $Al_2(SO_4)_3$, as its composition is very irregular and varies even in different parts of the same piece. According to Lunge and Keler,* the percentage of alumina in the commercial aluminium sulphate varies between 14·5 and 15·5 per cent. Al_2O_3 = 48·7 to 51·9 per cent. $Al_2(SO_4)_3$; in addition, this sample contained about 0·27 per cent. insoluble matter, 0·76 per cent. free sulphuric acid, a little sodium sulphate and iron compounds, mostly ferric salts and not exceeding 0·01 per cent. Fe. They found the quantities of iron should not exceed 0·001 per cent. for Turkey-red dyeing and 0·005 per cent. for steam-red and steam-pink.

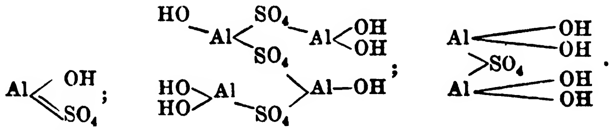
Basic aluminium sulphates are obtained, as indicated above, by adding alkalies or carbonates, &c., usually sodium carbonate, to the solutions of aluminium sulphate (or alum). The greater the amount of alkali added, the greater is the basicity of the product, as shown by the following equations:—

$$(1)\ Al_2(SO_4)_3 + Na_2CO_3 + H_2O = 2Al(SO_4)(OH) + Na_2SO_4 + CO_2.$$
$$(2)\ 2Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = Al_4(SO_4)_3(OH)_6 + 3Na_2SO_4 + 3CO_2.$$
$$(3)\ Al_2(SO_4)_3 + 2Na_2CO_3 + 2H_2O = Al_2(SO_4)(OH)_4 + 2Na_2SO_4 + 2CO_2.$$

A crystallised basic sulphate, $Al(SO_4)(OH)$, has been placed on the market by Messrs. Peter Spence & Co., Ltd.

The constitution of the basic salts is explained by the following formulæ:—

I. II. III.



With increasing basicity the salt becomes more similar to aluminium hydroxide; thus, formula I. shows a salt which is two-thirds a sulphate and one-third a hydroxide; while the salt in formula III. is only one-third a sulphate and two-thirds a hydroxide. By the increase of basicity, the intra-molecular cohesion is greatly diminished; the normal aluminium sulphate cannot be decomposed either by boiling or by diluting with water, the basic salt I. dissociates slowly and incompletely, salt II. more readily, and salt III. very fast on boiling or diluting with water, separating gelatinous aluminium hydroxide, $Al(OH)_3$.

Liechti and Suida † have investigated the nature of these salts; they experimented with solutions of the normal and basic salts, which were equivalent to a strength of 200 grms. normal aluminium sulphate, $Al_2(SO_4)_3 + 18H_2O$, per litre; they determined the effect which was produced both by boiling and by diluting with water, and they ascertained, besides, the quantities of alumina which were retained by the cotton fibre on steeping, drying, and ageing. A solution of normal aluminium sulphate —200 grms. per litre—could be boiled or diluted with water without any change, and yielded to the cotton fibre only 12·9 per cent. of its alumina; an equivalent solution of the first basic salt, $Al(SO_4)(OH)$, was precipitated after being boiled for some time, or on being diluted fourteen-fold with water, and gave up to the cotton fibre 51 per cent. of the available alumina; the more basic salt, $Al_4(SO_4)_3(OH)_6$, began to dissociate when heated to 68°, or when

* *Journ. Soc. Dyers and Col.*, 1895, p. 5. † *Journ. Soc. Chem. Ind.*, 1883, p. 537.

diluted with only twice its volume of water, and yielded as much as 58·7 per cent. of its alumina to the cotton fibre; finally, the most basic salt, $Al_2(SO_4)(OH)_4$, dissociated too rapidly on diluting to be available as a mordant. It was also found that the basic salts dissociated more rapidly when other sulphates—*e.g.*, sodium sulphate—were present in the solutions, which is, however, in contradiction with general experience. Henri Schmid, for instance, states that the basic salt, $Al_2SO_4(OH)_4$, is obtained in a sufficiently stable form if the alum or aluminium sulphate be mixed with about 20 per cent. of sodium or magnesium sulphate.* Possibly still more basic sulphates exist than those described here, which, however, are not soluble in water, and have not been prepared by precipitating aluminium sulphate with basic agents. D. Koechlin † has boiled a solution of aluminium acetate which contained basic aluminium sulphate, and thus produced a precipitate which contained for 100 parts sulphuric acid 343·5 parts alumina—*i.e.*, only $\frac{1}{10}$ of the sulphuric acid of the normal salt; whereas the soluble basic salt, $Al_2(SO_4)(OH)_4$, contains one-third the sulphuric acid that the normal salt does. Basic salts, like that produced by Koechlin, are probably formed by steeping cotton in commercial red liquor (which contains aluminium sulphate-acetates, as noticed below), and subsequently drying and ageing.

Liechti and Suida have tried to obtain pure basic sulphates by dissolving freshly-prepared aluminium hydroxide in a solution of the normal aluminium sulphate; they did not succeed, however, in obtaining very basic sulphates. On gradually adding aluminium hydroxide to the normal sulphate, sufficient to form the basic compound, $Al_4(SO_4)_3(OH)_6$, no alumina at all dissolved, and, on filtering, the solution was found to contain normal sulphate only, but no basic salt. It is supposed that the nascent basic compound became decomposed as follows:—$Al_4(SO_4)_3(OH)_6 = Al_2(SO_4)_3 + 2Al(OH)_3$.

Alum—*Potash Alum*, $Al_2K_2(SO_4)_4 + 24H_2O$; *Ammonia Alum*, $Al_2(NH_4)_2(SO_4)_4 + 24H_2O$.—The name "Alum" originally indicated the double sulphate of aluminium and potassium which crystallises in the shape of octahedra, with 24 molecules of water of crystallisation. The name was extended later to a whole class of double sulphates of analogous constitution and isomorphous form. In these either aluminium is substituted by another metal, which forms a sesquioxide analogous to alumina (Al_2O_3)—*i.e.*, by chromium, iron, or manganese; or potassium may be replaced by another monovalent metal; or both aluminium and potassium may be exchanged in this way. Thus a great number of "alums" are known; for instance—

Ammonia alum, ...	$Al_2(NH_4)_2(SO_4)_4 + 24H_2O$.
Soda alum, ...	$Al_2Na_2(SO_4)_4 + 24H_2O$.
Chrome alum, ...	$Cr_2K_2(SO_4)_4 + 24H_2O$.
Ferric-ammonia alum, ...	$Fe_2(NH_4)_2(SO_4)_4 + 24H_2O$.

All these alums crystallise in octahedra, and cannot be separated by crystallisation when present in solution together.

Commercial alums—*i.e.*, both potash alum and ammonia alum—are obtained by various processes, the ultimate aim of which is to produce a mixed solution of aluminium sulphate and potassium or ammonium sulphate. This mixture is allowed to crystallise, and is purified by recrystallisation.

Alum, as indicated, crystallises in large octahedra with 24 molecules of water of crystallisation. The solubility of potash and ammonia alum in water is given in the following table. Soda alum is much more soluble in

* See also F. Erban (*Zeitschrift für Farber-Industrie*, 1907, p. 332), who maintains that the mordant generally in use in Alizarin-red dyeing corresponds approximately to the formula $Al_2(SO_4)(OH)_4$.

† *Schuetzenberger*, *Farbstoffe*, II., p. 210.

water, but cannot easily be obtained in crystals; it is, consequently, not a commercial article. The alums are not soluble in absolute alcohol. 100 parts of water dissolve at—

	10° C.	20° C.	30° C.	40° C.	70° C.	100° C.
Parts potash alum, . .	9·5	15·1	22·0	30·9	90·7	357·5
Parts ammonia alum, .	9·1	13·6	19·3	27·3	72·0	421·9

Alum is not dissociated by boiling or by diluting with water. By the addition of caustic alkalies or alkaline carbonates to solutions of alum, so called "neutral" and "basic" alums are obtained, which are both analogous to the basic aluminium sulphates, and likewise decompose on boiling and on diluting. By gradually adding the alkali temporary precipitates are formed which redissolve on stirring, but become permanent on adding more alkali. A solution of alum which has been rendered as basic as possible without permanent precipitation is called by dyers "neutral alum"; it is, however, a basic salt. It can be prepared by boiling a solution of 12 parts of alum with 1 part calcium hydroxide. If it is allowed to evaporate slowly at the ordinary temperature, crystalline crusts are formed, which contain the basic salt, $Al_4(SO_4)_3(OH)_6$, and potassium sulphate (if potash alum was used). If the solution is heated above 40° C., ordinary alum and a precipitate of the composition, $Al_2(SO_4)(OH)_4 + K_2SO_4$, is obtained.

Alum is used by some dyers in preference to cake alum, since the crystalline form assures regular composition. It is, however, being gradually replaced by the latter, which is now sold at low prices in excellent qualities. Potash alum contains only 36·1 per cent. $Al_2(SO_4)_3$ = 10·76 per cent. Al_2O_3; and ammonia alum 37·7 per cent. $Al_2(SO_4)_3$ = 11·27 per cent. Al_2O_3; whereas, good brands of aluminium sulphate contain over 55 per cent pure $Al_2(SO_4)_3$ = over 16·4 per cent. Al_2O_3 (see also above, p. 224). No distinction is made in practice between potash and ammonia alum, but the latter is generally employed since it is cheaper; on the whole, both behave like aluminium sulphate.

Aluminium Chloride, $AlCl_3$ or Al_2Cl_6.—Aluminium chloride is obtained in solution by dissolving aluminium hydroxide in hydrochloric acid; this product contains water, which cannot be entirely removed without decomposition of the salt. By passing gaseous hydrochloric acid into the aqueous solutions, crystals having the composition $AlCl_3 + 6H_2O$ are obtained, which decompose readily by heat into hydrochloric acid, aluminium oxide or hydroxide, and water The solution is not decomposed either on boiling or on diluting with water. The article is sold in the form of a strong solution or in crystals (Peter Spence & Co., Ltd.)

Basic aluminium chlorides or *oxychlorides* are obtained by adding the requisite amount of sodium carbonate to the solution of the normal chloride. Liechti and Suida (*l.c.*) prepared the following basic chlorides in solution :—

(1) $Al_2Cl_5(OH) = AlCl_3 + AlCl_2(OH)$. (3) $Al_2Cl_3(OH)_3 = AlCl_2(OH) + AlCl(OH)_2$.
(2) $Al_2Cl_4(OH)_2 = 2AlCl_2(OH)$. (4) $Al_2Cl_2(OH)_4 = 2AlCl(OH)_2$.

None of these solutions is dissociated either by heating or diluting with water. By dissolving aluminium hydroxide in aluminium chloride only the first two basic salts could be obtained. To a solution of aluminium chloride a quantity of aluminium hydroxide was added, sufficient to form the basic salt, $AlCl_2OH$. The alumina dissolved only on heating, and the solution remained clear on cooling. To this clear solution a further quantity of

aluminium hydroxide was added, sufficient to form the compound $AlCl(OH)_2$. No more alumina, however, could be made to dissolve, the precipitate even increased, and on filtering it was found that the solution contained 1 equivalent of hydrochloric acid, HCl, for 2 equivalents of aluminium chloride, $AlCl_3$. A similar behaviour was shown by aluminium sulphate (see above).

The aluminium chlorides yield but small quantities of alumina to the fibre, and are rarely used as mordants. A process of carbonising vegetable matter in wool is based on the property which aluminium chloride has of decomposing when its aqueous solution is evaporated to dryness. Woollen tissues are simply saturated with a solution of normal aluminium chloride and dried after the excess of liquid has been removed by mechanical means; the hydrochloric acid which is liberated destroys the vegetable fibre without affecting the colours. Aluminium chloride has antiseptic properties, and has been recommended as a disinfectant.

Aluminium Hypochlorite, $Al(ClO)_3$ (?)—*Wilson's Bleaching Liquor.*—Aluminium hypochlorite is obtained in solution by the double decomposition of aluminium sulphate and chloride of lime solutions. The compound is very prone to decompose into aluminium chloride and oxygen, and can be used as a bleaching agent without any acid being added. Four parts of aluminium hypochlorite (calculated on $Al(ClO)_3$) are diluted with 200 parts of water, and the goods steeped in this solution for two to three hours. The compound has also been recommended as a mordant, since it decomposes on the fibre into aluminium hydroxide and hypochlorous acid—$Al(ClO)_3 + 3H_2O = Al(OH)_3 + 3ClOH$. On the whole, this substance offers no special advantage for the bleaching and dyeing of the textile fibres, and the fact that it readily decomposes is counterbalanced by the generation of aluminium chloride which easily destroys the vegetable fibre. The antiseptic properties of aluminium chloride, however, render it available for other manufactures—*e.g.*, paper making.

Aluminium Nitrate, $Al(NO_3)_3$.—This salt is obtained by dissolving aluminium hydroxide in nitric acid, or by double decomposition of the sulphate with nitrate of lead or barium. The salt forms crystals with 9 molecules of water, which are very soluble and deliquescent, and when heated to 150° are decomposed into nitric acid, aluminium oxide, and water.

Basic aluminium nitrates can be obtained by adding the requisite quantities of sodium carbonate to the solution of the normal salt; neither the normal nor the basic aluminium nitrates are dissociated by heating or by diluting with water. Aluminium nitrate has a limited application in the production of steam colours on calico; it is not used as a mordant for wool or silk.

Aluminium Sulphite, $Al_2(SO_3)_3$ (?); **Aluminium Bisulphite,** $Al(SO_3H)_3$ (?).—Aluminium sulphite or bisulphite is obtained by dissolving aluminium hydrate in a strong solution of sulphur dioxide in water (sulphurous acid). The solutions are readily decomposed on boiling.

Aluminium Thiosulphate (*Hyposulphite*).—This salt is obtained by double decomposition of aluminium sulphate and calcium thiosulphate. It is known in solution only, and its exact composition has not been determined.

Aluminium thiosulphate was prepared by E. Kopp as early as 1856. He found that the aqueous solution readily decomposes on boiling, into aluminium hydroxide, sulphur dioxide, and sulphur; and recommended it to calico printers as a mordant, its advantages being that it was cheaper than aluminium acetate; that it fixed the alumina better on the fibre than the other salts; and that it prevented, by its reducing action, the oxidation and fixation of iron on the fibre. This mordant, however, has not found general application, since it gives off sulphur dioxide even on drying on the cylinders, and deposits sulphur together with the alumina on the fibres; hence its employment is not advisable.

A solution containing alum and sodium thiosulphate has been proposed for mordanting silk previous to dyeing with the Alizarins. It is said to have yielded good results on a large scale.

Aluminium Thiocyanate or Sulphocyanide, $Al(CNS)_3$.—Aluminium thiocyanate is obtained by the double decomposition of aluminium sulphate with barium or calcium thiocyanate—$Al_2(SO_4)_3 + 3Ba(CNS)_2 = 2Al(CNS)_3 + 3BaSO_4$. Care must be taken that the aluminium sulphate does not contain any excess of acid; if it does, it must be neutralised by an alkaline thiocyanate, preferably sodium or ammonium thiocyanate. Sulphuric acid in the free state would be liable to cause a tendering of the fibre on drying and steaming, and to carry iron into the colour, whereas the neutral thiocyanates do not affect the fibres nor exert a corroding action on iron. Aluminium thiocyanate of 32° Tw. strength is made by dissolving the following ingredients at 60° C.:—

3 kgs. (30 lbs.) cake-alum in
2·5 litres (2½ galls.) water;
and
4·1 kgs (41 lbs) barium thiocyanate in
2·5 litres (2½ galls.) water.

Mix the two solutions, filter from the white precipitate, wash with water, dilute with the washing liquor till the strength is 32° Tw.

The crude calcium thiocyanate solutions can also be used—

5 kgs. (10 lbs) cake-alum are dissolved in
5 litres (1 gall) boiling water, then
250 grms. (½ lb) chalk, and
11½ litres (2$\frac{3}{10}$ galls) calcium sulphocyanide 32° Tw. are added.

If necessary the mordant can be concentrated by boiling over a fire.

Liechti and Suida examined the normal and basic aluminium thiocyanates. The normal salt can be boiled, and even concentrated by boiling, to a syrupy consistency without being decomposed. The salt, $Al_2(CNS)_5OH$, is also stable; but the more basic salts are decomposed when boiled; mere dilution with water will not cause the decomposition of any of these salts.

Aluminium thiocyanate was introduced by Storck for the production of Alizarin reds in calico-printing as a substitute for aluminium acetate. It possesses the great advantage that it does not attack the steel doctors of the printing machine, and thus does not introduce iron into the printing colour; hence the purity and brilliancy of Alizarin red is preserved. The high price of the article has prevented its more general employment, especially in wool dyeing. Very fine results are obtained by mordanting this fibre with aluminium thiocyanate. The wool is introduced into the cold mordanting bath, which is gradually heated to boiling during one to one and a-half hours. Silk may be mordanted like wool. The thiocyanate is also used in silk-printing.

Aluminium Acetate, $Al(C_2H_3O_2)_3$ or $Al_2(C_2H_3O_2)_6$.—Normal aluminium acetate is not known in the pure state. The solution is obtained by dissolving aluminium hydroxide in acetic acid, or by the double decomposition of aluminium sulphate and lead, or calcium acetate—$Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 = 2Al(C_2H_3O_2)_3 + 3PbSO_4$. The solution of normal aluminium acetate smells of acetic acid, and yields, on heating or prolonged standing, the basic acetate, $Al(C_2H_3O_2)_2(OH)$, in the solid state, but containing various amounts of water, according to the different conditions under which it is formed.

Solutions of the normal acetate which contain other salts (like the alkaline sulphates or chlorides or alum) become turbid when heated, and form precipitates when boiled much more readily than the pure acetate; they dissociate, forming acetic acid in the free state, and precipitates of basic acetates, which redissolve on cooling, unless the acetic acid has been driven off by prolonged

boiling. These results, which were obtained many years ago by Walter Crum,* are not in harmony with the more recent researches of Liechti and Suida (*l.c.*). The latter state that normal aluminium salts are not dissociated either by heating or by diluting with water.

By adding to the solution of normal aluminium acetate the requisite amounts of sodium-carbonate solutions of basic acetates of varying basicity are obtained, as shown by the following equations:—

$$4Al(C_2H_3O_2)_3 + Na_2CO_3 + H_2O = 2Al_2(C_2H_3O_2)_5(OH) + 2NaC_2H_3O_2 + CO_2.$$
$$2Al(C_2H_3O_2)_3 + Na_2CO_3 + H_2O = 2Al(C_2H_3O_2)_2(OH) + 2NaC_2H_3O_2 + CO_2.$$
$$4Al(C_2H_3O_2)_3 + 3Na_2CO_3 + 3H_2O = 2Al_2(C_2H_3O_2)_3(OH)_3 + 6NaC_2H_3O_2 + CO_2.$$
$$Al(C_2H_3O_2)_3 + Na_2CO_3 + H_2O = Al(C_2H_3O_2)(OH)_2 + 2NaC_2H_3O_2 + CO_2.$$

The solutions of basic acetates are dissociated on heating; the more basic they are the lower is the temperature at which the dissociation begins; but the dissociation is retarded by dilution with water; in the absence of alkaline sulphates no dissociation is effected by diluting with water at the ordinary temperature. The precipitates formed by basic acetates in the absence of sulphates at higher temperatures are not redissolved on cooling. They seem to consist chiefly of aluminium hydroxides.

Comparative experiments were made by Liechti and Suida as to the mordanting power of normal and basic acetates. They used solutions of $Al(C_2H_3O_2)_3$ and $Al(C_2H_3O_2)_2(OH)$, equivalent to 200 grms. normal sulphate per litre, and impregnated pieces of calico with such solutions until the cloth had taken up an amount of the respective solutions equal to its own weight; the cloth was then dried, aged, and washed in equal quantities of water to remove all the aluminium which had not been fixed; under these circumstances only one-half of the alumina in the normal salt, while all that in the basic salt was taken up in the fixing.

In the presence of alkaline sulphates—*e.g.*, sodium sulphate—both the normal and the basic aluminium acetates are dissociated by diluting with water, and the dissociation by heat proceeds more readily than in the absence of sulphates. The precipitates obtained by heating redissolve on cooling if formed in the presence of soluble sulphates. The acetates which are obtained from alum and lead or calcium acetate, always contain soluble sulphates, as shown by the equation—$Al_2K_2(SO_4)_4 + 3Pb(C_2H_3O_2)_2 = 2Al(C_2H_3O_2)_3 + K_2SO_4 + 3PbSO_4$. In practice the basic acetates are prepared by the double decomposition of aluminium sulphate partly with acetate of lead or calcium, partly with sodium carbonate, as is indicated by the following equation—

$$Al_2(SO_4)_3 + Na_2CO_3 + 2Pb(C_2H_3O_2)_2 + H_2O = 2Al(C_2H_3O_2)_2(OH) + Na_2SO_4 + 2PbSO_4 + CO_2.$$

Both in this case, and when the acetate is prepared from alum, the product contains a soluble sulphate, and is thereby more easily dissociated.

It appears that the precipitates which are formed in the presence of sulphates always contain some sulphuric acid, and consist of a very basic sulphate (see p. 226—the analysis of D. Koechlin).

A crystallised basic aluminium acetate, $Al_2(C_2H_3O_2)_4(OH)_2$, containing 86 per cent. of this salt and 14 per cent. sodium sulphate is supplied by E. de Haen, Chemical Works List at Seelze, near Hanover.

Aluminium acetates, which are prepared with lead acetate, are liable to retain in solution some lead in the form of lead sulphate, which may exert an injurious influence; therefore, in certain cases (for instance, in steam Alizarin reds), the lead acetate is replaced by calcium acetate. Lead sulphate, however, although perceptibly soluble in aluminium acetate, is found only in traces

* *Liebig's Ann.*, lxxxix., p. 156.

in solutions which contain soluble sulphates—such as those of sodium or aluminium.

Aluminium Sulphate-Acetates or Sulpho-Acetates.—171 parts of crystallised lead acetate are required to convert 100 parts of aluminium sulphate into normal aluminium acetate; and for 100 parts of potash alum or ammonia alum 120 and 125 parts respectively of the lead salt are required, in conformance with the two equations*—

$$(1) \quad Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 = 2Al(C_2H_3O_2)_3 + 3PbSO_4.$$
$$(2) \quad Al_2(NH_4)_2(SO_4)_4 + 3Pb(C_2H_3O_2)_2 = 2Al(C_2H_3O_2)_3 + 3PbSO_4 + (NH_4)_2SO_4.$$

In practice a very much smaller amount of lead acetate is usually employed, and this is still further reduced, if a part of the sulphuric acid is neutralised by the addition of soda or chalk, to produce a basic salt. Thus mixtures of normal or basic sulphates and of normal acetate of aluminium are obtained, which are known as *sulphate-acetates* or *sulpho-acetates.* The investigations of D. Koechlin (-Schouch) have proved—in harmony with long practical experience—that these aluminium sulphate-acetates deposit in the cotton fibre by impregnating, and subsequent ageing, basic sulphates which possess the same mordanting properties as the hydroxides of aluminium. A precipitate of pure basic aluminium sulphate was prepared from alum, dissolved in acetic acid, and fixed on the fibre by impregnating and ageing. The compound which was deposited in the fibre in this way must be a basic aluminium sulphate, according to the method of its preparation. Its value for dyeing was ascertained by a practical dye test with madder, and it proved, indeed, an excellent mordant.

Investigations of Liechti and Suida (*l.c.*) confirm this opinion. These authors prepared sulphate-acetates in accordance with the following equations*:—

$$(1) \quad Al_2(SO_4)_3 + Pb(C_2H_3O_2)_2 = 2Al(SO_4)(C_2H_3O_2) + PbSO_4.$$
$$(2) \quad 2Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 + Na_2CO_3 + H_2O = 2Al_2(SO_4)(C_2H_3O_2)_3(OH) + 3PbSO_4 + Na_2SO_4 + CO_2.$$
$$(3) \quad Al_2(SO_4)_3 + Pb(C_2H_3O_2)_2 + Na_2CO_3 + H_2O = Al_2(SO_4)(C_2H_3O_2)_2(OH)_2 + PbSO_4 + Na_2SO_4 + CO_2.$$
$$(4) \quad Al_2(SO_4)_3 + C_2H_4O_2 + 2Na_2CO_3 + H_2O = Al_2(SO_4)(C_2H_3O_2)(OH)_3 + 2Na_2SO_4 + 2CO_2.$$

The normal sulphate-acetate, $Al(SO_4)(C_2H_3O_2)$, does not dissociate when diluted with water, although, when heated, the basic sulphate-acetates are decomposed by both agencies, while increase in basicity lowers the dissociation point both on heating and on diluting. The precipitates are formed as jelly-like substances at temperatures from 89° to 40° C. The precipitate of the normal sulphate-acetate redissolves on cooling the solution, that of $Al_2(SO_4)(C_2H_8O_2)_3OH$ partially; whereas the precipitates formed by heating the more basic sulphate-acetates are permanent. All these sulphate-acetates—normal and basic—yield nearly the whole of their alumina to the fibre during mordanting, drying, and ageing; and, therefore, in this respect they are much stronger mordants than the sulphates.

Red Liquor.—The commercial solutions of acetates and sulphate-acetates of aluminium are known in the trade as *red liquor*, because they are employed by cotton dyers and calico printers as mordants for Alizarin reds. The composition of the red liquors varies greatly, and their value for different styles of work is better determined by practical tests than by analysis. They are

* In these equations the water of crystallisation—18 equivalents for aluminium sulphate, and 3 equivalents for lead acetate—have been omitted; they must be taken into account in calculating the proportions for practical purposes.

prepared by the double decomposition of normal aluminium sulphate and commercial acetate or pyrolignite of lime, with or without addition of chalk or soda, and have always a yellowish-brown appearance from the presence of empyreumatic substances; their strength varies from 1·08 to 1·12 specific gravity.

Lauber * gives the following proportions for the preparation of red liquor:—

1.	2.
189 kgs. (189 lbs.) alum,	40 kgs. (40 lbs.) cake-alum,
161 kgs. (161 lbs.) yellow sugar of lead, and	50 kgs. (50 lbs.) yellow sugar of lead,
450 litres (45 galls.) water.	1½ kgs. (1½ lbs.) chalk, and
	90 litres (9 galls.) water.

Aluminium Chloride-Acetate, $AlCl(C_2H_3O_2)_2$.—Liechti and Suida prepared a salt of this composition according to the following equation:—

$$Al_2(SO_4)_3 + 2Pb(C_2H_3O_2)_2 + BaCl_2 = 2AlCl(C_2H_3O_2)_2 + 2PbSO_4 + BaSO_4.$$

They found that this salt does not dissociate either on heating or on diluting, and yields to the cotton fibre by steeping, drying, and ageing the remarkably low amount of 3·26 per cent. alumina.

Aluminium Nitrate-Acetate, $Al(NO_3)(C_2H_3O_2)_2$, is obtained by double decomposition of aluminium sulphate with the acetate and nitrate of calcium or lead, and is used as a mordant for calico-printing and silk dyeing. It is valuable for the production of fine steam Alizarin reds, since it is very gradually dissociated on steaming.

Aluminium Oxalate, $Al_2(C_2O_4)_3$ (?).—Aluminium oxalate in the pure state has not been prepared.

Aluminium hydroxide dissolves in oxalic acid; the solution yields, on evaporating, an amorphous, deliquescent mass. The solutions of aluminium salts are not precipitated by oxalic acid or its salts. Aluminium oxalate, obtained by dissolving the hydroxide in oxalic acid, is limited in its use to certain steam colours for calico-printing. If oxalic acid is used in mordanting wool with aluminium sulphate, the oxalate is formed to some extent, and takes part in the mordanting process. The oxalate itself, however, is not used in wool or silk dyeing. Regarding the behaviour of aluminium oxalate as a wool-mordant (see pp. 236 and 237).

Aluminium Tartrate.—This salt has not been prepared yet in the pure state, although it is a very important substance in wool dyeing, being formed by the double decomposition of aluminium sulphate and acid potassium tartrate (tartar) in the mordanting bath (see pp. 236 and 237).

Aluminium hydroxide, dissolved in tartaric acid, is also used in a few steam colours in calico-printing.

APPLICATION OF THE ALUMINIUM SALTS TO THE TEXTILE FIBRES.

Aluminium sulphate and alum are often used as mild acidifying agents, instead of sulphuric acid, in the dye-bath—*e.g.*, in the dyeing of Soluble blue on cotton and of acid colours on wool. If so employed, they cannot be considered as mordants in most cases, none of their constituents becoming parts of the ultimate colour.

Aluminium salts render the textile fibres water-repellent, and are, therefore, used to a great extent for water-proofing. Aluminium acetate is most generally employed and the fibre may simply be impregnated with pure normal or basic acetate and dried. More generally the fabric is treated for

* *Handbuch des Zeugdrucks.*

some hours in a warm solution of aluminium acetate 8° to 10° Tw., and subsequently passed through a soap solution containing 50 to 75 grms. soap per litre (8 to 12 ozs. per gallon) and heated to about 45°; after this the goods are well dried in a hot drying chamber and finally calendered, which presses the fibre together and thus assists the water-proofing. Such substances as Japan wax, gums, oils, paraffin, &c., are frequently added to the soap-bath to give a better water-repellent resistance to the fabric.

Application to Cotton and Linen—(1) *Aluminium Sulphate and Alum.*—Normal aluminium sulphate and alum yield but very little alumina to the fibre (13 per cent. according to Liechti and Suida, see p. 225). They are used for the mordanting of cotton in exceptional cases only, as, for instance, when a dyestuff of great tinctorial power is used. The cotton is impregnated with a solution of alum, wrung, passed without washing through a solution of sodium carbonate at 50° to 60° C. for twenty minutes, and thoroughly washed in water. Use for 10 kgs. (10 lbs.) cotton, 1 kg. (1 lb.) alum, and ½ kg. (½ lb.) soda crystals in 200 litres (20 galls.) water. Methyl violet yields on this mordant brighter, though less fast, shades than on tannin and antimony.

The basic salts are usually employed for the mordanting of cotton with aluminium sulphate. The basic sulphate corresponding to the formula $Al(SO_4)(OH)$ is prepared by dissolving 2 kgs. (6 lbs.) pure aluminium sulphate $(Al_2(SO_4)_3 + 18H_2O)$ in 10 litres (3 galls.) water, and adding gradually a cold solution of 330 grms. (1 lb.) soda ash (58°) in 2½ litres (3 quarts) water. During the mixing the mass is vigorously agitated by stirring, and fresh portions of soda are added only after the precipitate first formed has redissolved. The solution is diluted to about 10° to 12° Tw. To obtain the compound free from other salts, the aluminium sulphate can be completely precipitated as the hydroxide, washed, and redissolved in diluted sulphuric acid; for 2 kgs. (10 lbs.) aluminium sulphate, 1 kg. (5 lbs.) soda ash (58°), and 600 grms. (3 lbs.) sulphuric acid (168° Tw.) are necessary. In case the alum-cake should contain more or less than 51·35 per cent. $Al_2(SO_4)_3$—as demanded by the formula $Al_2(SO_4)_3 + 18H_2O$—more or less is used to obtain exactly the same product; if it contains an excess of sulphuric acid a correspondingly larger amount of soda ash is employed.

According to Henri Schmid, the salts, $Al_2SO_4(OH)_4$ and $Al_4(SO_4)_3(OH)_6$, and the salts lying between these two, are chiefly used for mordanting; they are made stable enough by addition of sodium- or magnesium sulphate, and then readily decompose in the fibre so as to be fixed either by drying or by chemical agents (chalking or dunging).

Two essentially different methods are employed in mordanting cotton with basic aluminium sulphate:—

(1) The material is impregnated directly with the mordant and the latter fixed by other chemicals or by ageing.

(2) The material is first impregnated with a substance which attracts the basic sulphate and forms an insoluble compound with alumina (oil mordants, tannic acid), or which deposits alumina in an insoluble form in the fibre by double decomposition (stannate of soda); after this treatment follows the mordanting with basic aluminium sulphate or alum; a further fixing of the alumina mordant is sometimes necessary.

Direct Mordanting with Basic Aluminium Sulphate.—The cotton is turned for some time in the above-described solution of the basic sulphate and left in the bath for three to five hours, wrung, and dried. More alumina is fixed if the impregnating of the material with the mordant is followed by ageing. The vegetable fibre, however, is liable to be weakened by the free acid or acid salts of aluminium which are formed thereby. Loose cotton or cotton yarn would, besides, give uneven shades through unequal drying, and, consequently,

unequal decomposition of the basic salt. For these reasons, it is preferable to impregnate the goods with basic sulphate and to pass them subsequently through the solution of a salt which is capable of fixing the alumina on the fibre, either by precipitating it in the free state or by combining with it in the form of an insoluble salt (*e.g.*, arsenate of soda). A great number of fixing agents have been referred to on previous pages and are actually used under different conditions. The material which has been impregnated with the basic aluminium sulphate is wrung out, dried at a low temperature, and worked for half an hour in the lukewarm fixing bath. After a thorough washing it is ready for dyeing. The fixing liquor is prepared so that each litre (10 galls.) shall contain 5 to 10 grms. (½ to 1 lb.) of either of the following salts:—Arsenate, phosphate, or silicate (100° Tw.) of soda, sodium carbonate, ammonium carbonate, or chalk; of ammonia liquor about 50 grms. per litre (½ lb. per gallon) are used; a soap solution containing 1 per cent. neutral soap is also sometimes employed; the application of cow-dung has been previously explained under *Ammonium Carbonate.*

Mordanting with Basic Aluminium Sulphate after Previous Impregnation of the Cotton with other Substances.—The process of mordanting cotton with olive oil or sulphated oil, also with tannic acid, and subsequently with basic sulphate of aluminium is employed, notably in Turkey-red dyeing, and will be fully described under that heading.

For other colours, the cotton is impregnated with a solution of about 100 grms. neutralised Turkey-red oil per litre (1 lb. per gallon), wrung or squeezed, dried in a stove, and worked for half an hour in the previously described solution of basic aluminium sulphate (10° to 12° Tw.); after this the cotton is washed in water and passed through a weak soap-bath (1 part of soap in 1,000 parts of water) to fix the alumina thoroughly and to remove all excess of mordant. A final thorough rinsing in water makes the material ready for dyeing. In place of Turkey-red oil an equal amount of neutral soap may be employed. Tannic acid is used in a similar way.

For certain colours, especially the Eosins, cotton is steeped in a tepid solution of stannate of soda for two to three hours, wrung evenly, steeped for two to three hours in partially neutralised alum, wrung again, and dyed without washing. For 10 kgs. (10 lbs.) of cotton, ½ kg. (½ lb.) stannate of soda, ½ kg. (½ lb.) alum, and 100 grms. (1½ ozs.) soda crystals are used.

The composition of the mordant which is retained by the fibre varies with the different fixing processes. In almost every case aluminium hydroxide is formed either by mere dissociation of the aluminium salt, or by decomposition of the same with ammonia, or with sodium or ammonium carbonate, or with chalk, &c. In addition, arsenate and phosphate of soda generate more or less aluminium arsenate and phosphate; soap produces stearate, palmitate, or oleate of aluminium; whereas silicate of soda forms the hydroxide only. If the material was prepared with tannic acid, oil or soap, tannate, &c., of aluminium is formed; the mordanting with stannate and alum produces only stannic hydrate and aluminium hydroxide. In case a basic sulphate is fixed exclusively by ageing, very basic sulphates are formed, which, being insoluble in water, are retained, together with the hydroxide, while the neutral sulphate and free acid, which were formed by dissociation through ageing, are removed by washing. It is, however, more usual to pass the goods after the ageing through some fixing bath—*e.g.*, chalk or phosphate—which remove probably the whole amount of the sulphuric acid

(2) *Aluminium Acetate and Sulphate-Acetate; Red Liquor.*—These mordants are not extensively used by the ordinary cotton dyer, since they are more costly than the basic sulphates, and possess no advantage over these in the general methods of fixing by precipitation. They can, however, be employed

exactly like the basic sulphates, and are frequently used by Turkey-red dyers to replace the sulphates entirely or in part. Goods which have been impregnated with the acetates and sulphate-acetates must not be dried at high temperatures, since these compounds are most readily dissociated on the fibre by heat, when acetic acid escapes and the base remains on the fibre in a form which renders it less capable of combining with the colouring matter in the subsequent dye-bath; poor and irregular colours would thus result. This fact may be due to the generation of aluminium oxide instead of the hydroxide, as shown by either of the following equations:—

$$(1) \quad 2Al(C_2H_3O_2)_3 + 3H_2O = Al_2O_3 + 6C_2H_4O_2.$$
$$(2) \quad 2Al(C_2H_3O_2)_2(OH) + H_2O = Al_2O_3 + 4C_2H_4O_2.$$

Another explanation is that a basic acetate or a less hydrated aluminium hydroxide is formed, neither of which forms colour lakes. Mordants that have been spoiled by overheating are said to have been "burned."

In the ordinary course of treatment the mordanted goods are not always passed directly into the fixing bath, but are first subjected to the so-called *ageing process*, which has already been mentioned several times. The ageing consists in exposing the mordant in the fibre to the action of warm and moist air. In the case of aluminium acetate, the object of the ageing process is to decompose the salt, and to deposit the base in the hydrated form in the fibre, the acid being partially or wholly volatilised:—

$$Al(C_2H_3O_2)_3 + 3H_2O = Al(OH)_3 + 3C_2H_4O_2.$$

Aluminium acetates in which a part of the acetic acid has been replaced by other acids, especially sulphuric acid, yield richer colours by the ageing process than the pure acetate, the latter being probably decomposed too rapidly. Aluminium sulphate-acetate, $Al_2(SO_4)(C_2H_3O_2)_3OH$, seems to give the most satisfactory results, and to yield nearly the whole of its aluminium to the fibre. In this case, as with basic aluminium sulphate, a very basic aluminium sulphate in an insoluble state is fixed together with aluminium hydroxide. A similar salt seems to be fixed, if an aluminium acetate which contains another soluble sulphate is subjected to ageing.

With the chemical fixing agents like ammonia, arsenate of soda, &c., the red liquor mordants yield the same products as the sulphates of alumina.

The acetates and sulphate-acetates of aluminium are principally employed by calico-printers. The acetates are used in steam colours when dyestuff and mordant are printed on the cloth together in the form of a mechanical mixture, and the colour is "developed" on or in the cloth by "steaming;" the normal acetate is generally used, and acetic acid in the free state is added to the colours to prevent a premature decomposition of the mordant. The sulphate-acetates are employed when the cloth is first mordanted, and then subjected to the ageing process, the dyeing process following.

Certain basic colours, especially Victoria blue and Night blue, are dyed in conjunction with aluminium acetate on cotton which has been previously mordanted with tannin and antimony. During the gradual raising of the temperature the acetate is dissociated in the fibre, and the hydroxide in the nascent state attracts some of the colouring matter.

The other aluminium salts are not frequently used as mordants on cotton. They have been fully described before. As to aluminate of soda, see p. 222.

Application to Jute.—Jute, as a rule, is dyed without mordants. Aluminium sulphate and alum are used as acidifying agents for the dyeing with acid dyestuffs in the same way as in wool dyeing. In many cases, either of the two salts is added to the dye-bath, together with, or without acetic, tartaric, or sulphuric acid. For some colours jute is boiled in alum solution, and passed

through carbonate of soda before dyeing. This is sometimes done for certain azo-colours, like Scarlet 3 R, which are too easily soluble in an acid bath to dye well.

Application to Wool.—Wool essentially differs from cotton in its behaviour towards the aluminium salts, and is mordanted in a totally different way. The investigations of Liechti and Schwitzer* have thrown much valuable light on the reactions which take place in mordanting wool.

Experiments have shown that wool takes up sulphuric and hydrochloric acid in the free state, retaining them with such force that they are only imperfectly removed by repeated boiling out with water.

In a similar manner salts are taken up. The wool fibre possesses both basic and acid character, and seems to dissociate the salts by combining both with the acid and with the base, the base being taken up either in the free state or in the form of a basic salt. This reaction takes place most completely at the boiling point. Aluminium sulphate, for instance, is most readily decomposed by the wool fibre into basic sulphates and free acid, especially at or near the boiling temperature. The alumina which is thus taken up is retained in an insoluble form with considerable force by the fibre; no fixing agents are required, as is the case with cotton; the fixation takes place simultaneously with the impregnation in the mordanting bath under the influence of the elevated temperature. The basic salts, which are fixed on the fibre, undergo a further decomposition by washing with water; they lose acid, and become more basic, while the acid is removed by the wash water.

The wool fibre attracts, also, finely-divided precipitates from liquids, and retains them with great energy. This power of attraction is comparatively weak in cold liquids, but it increases with the temperature, so that considerable amounts of such precipitates can be attached to the wool by prolonged boiling, although not fast enough to resist washing and rubbing. By the action of the wool fibre on aluminium sulphate, a precipitate of basic aluminium sulphate may be produced and boiled on to the wool fast enough to resist washing with water, although it is only mechanically fixed on the surface of the fibre. These superficially fixed mordants produce in dyeing colour lakes, which adhere still more loosely to the surface of the fibre, and possess in a high degree the defect of rubbing.

On the contrary, mordants which have entered into an intimate combination with the substance of the fibre are less liable to produce colour lakes which rub off. To attain this end the mordanting salt must possess a certain resistance to the dissociating action of the wool, so as to allow of its penetrating into the interior of the fibre before it is decomposed and fixed, and of the dissociation and absorption taking place simultaneously, without the intermediate formation of a precipitate in the liquor, which might be attracted and mechanically fixed by the wool.

Taken as a whole, the salts of oxalic and tartaric acid fulfil these conditions best—a fact that reminds us of the property of the non-volatile organic acids to impede the precipitation of aluminium hydroxide by alkalies or other agents.

On the other hand, the basic aluminium sulphates are entirely unsuitable for the mordanting of wool, because they dissociate before they are taken up by this fibre.

Liechti and Schwitzer have compared *the action of sulphate, oxalate, and tartrate of aluminium in mordanting*. They prepared solutions of aluminium oxalate, $Al_2(C_2O_4)_3$, and of aluminium tartrate, $Al_2(C_4H_4O_6)_3$, by dissolving 2 equivalents of aluminium hydroxide, $Al(OH)_3$, in 3 equivalents of oxalic and tartaric acid respectively. If wool is boiled in a solution of *normal aluminium sulphate* the bath becomes exhausted if less than 5 per cent.

* *Journ. Soc. Dyers and Col.*, 1886, p. 161.

sulphate (of the weight of the wool) is used. Larger amounts leave increasing proportions in the liquor. The mordanting baths become turbid on boiling by separating an insoluble basic aluminium salt. A part of the precipitate thus formed becomes mechanically fixed, and is removed on washing, the wash waters being turbid; a part remains in the mordanting liquor. The wool which has been mordanted gives an acid wash water on treatment with boiling water—thus proving that the aluminium sulphate has been decomposed, and that not merely alumina but free acid has been extracted from the mordanting bath. If *sulphuric acid is added to the mordanting bath,* the decomposition of the mordant is less rapid, and it is better fixed than when the normal sulphate is used alone. Comparatively large quantities of sulphuric acid are necessary—more than 3 equivalents H_2SO_4 of the sulphate, $Al_2(SO_4)_3$, and the effect of the acid decreases with an increasing dilution of the bath.

Alum is a somewhat less efficient mordant than aluminium sulphate; this is evidently due to the dissociating effect which is exerted by the alkaline sulphates present in the former salt.

Normal aluminium oxalate, $Al_2(C_2O_4)_3$, is almost completely taken up from the mordanting bath. A smaller amount of precipitate remains in the liquor, and less can be removed from the wool than in the case of mordanting with the normal sulphate. The wool, on treatment with boiling water, gives, in this case also, an acid wash water.

Normal aluminium tartrate, $Al_2(C_4H_4O_6)_3$, if used as the wool mordant, leaves scarcely any precipitate in the bath, and does not give up any to the wash water. On treatment with hot water, the wool imparts also to the latter an acid reaction. Boiling water does not remove the mordant proper. Wool which had been boiled out several times with distilled water after mordanting, gave, on dyeing with Alizarin, more brilliant and fuller colours than wool which had been simply rinsed in water.

The normal tartrate can be replaced, with excellent results, by a mixture of 1 equivalent of aluminium sulphate and 3 equivalents of tartar (acid potassium tartrate) — $Al_2(SO_4)_3 + 3KC_4H_5O_6 = Al_2(C_4H_4O_6)_3 + 3KHSO_4$. In this case, as shown by the equation, a mixture of normal aluminium tartrate and acid potassium sulphate is formed.

If the normal tartrate is prepared by double decomposition—*e.g.*, with normal potassium-sodium tartrate (Rochelle salt), as in the following equation:—

$$2Al_2(SO_4)_3 + 6(KNaC_4H_4O_6) = 2Al_2(C_4H_4O_6)_3 + 3K_2SO_4 + 3Na_2SO_4,$$

the results obtained are not as good as those with the pure tartrate or with the mixture produced with tartar. These facts lead to the conclusion that the tartrate is similar to other aluminium salts, and is more rapidly dissociated in the presence of alkaline sulphates than in the pure state; and that in the case of a mixture of aluminium sulphate and tartar being used, the acid sulphate prevents a premature dissociation.

An examination of the spent mordant- and dye-baths shows that the mordanting is most perfect in the case of the tartrate, the whole of the alumina being fixed in a permanent manner.

It appears that not only the hydroxides but also true basic aluminium salts are deposited by the mordanting process in the fibre, as on dyeing the well-washed wool with Alizarin, the spent dye liquors invariably show an acid reaction.

These theoretical considerations and experiments are in perfect harmony with practical experience.

Basic aluminium sulphates are not used as wool mordants, neither are the acetates nor sulphate-acetates, as they dissociate too rapidly and give poor results. By depositing too much of the mordant on the surface, they make

the wool harsh and give rise to uneven dyeing and rubbing. Thiocyanate of aluminium, which is not as sensitive as the acetates, is a very good wool mordant; but its general employment is prevented by its high price.

The aluminium mordant *par excellence* for wool is aluminium sulphate, either alone or in conjunction with acids or acid salts. In some cases the sulphate is used without any additions. Most generally, however, a mixture of the sulphate with tartar or tartar substitutes is required to obtain full and brilliant colours which do not rub off. These tartar substitutes are mostly sodium bisulphate or oxalates, or they consist of tartar which has been prepared with sufficient sulphuric acid to convert all the potassium into potassium sulphate (see p. 164). From the foregoing it appears that none of these "substitutes" can replace the tartar completely, because the action of the latter depends on the formation of *aluminium tartrate by double decomposition*. They have, of course, some effect, as has also sulphuric acid. For a full shade about 6 to 8 per cent. aluminium sulphate and 5 to 7 per cent. tartar (of the weight of the wool) are necessary. The quantity of tartar may be reduced to about half this amount, or it may be partly or even wholly replaced by sulphuric, hydrochloric, oxalic acid, bisulphate of sodium, &c., with very good, although not equally fine, results. About 4 per cent. of sulphuric acid (of the weight of the wool) is used, if the amount of water does not exceed 50 to 60 times the weight of the wool; otherwise more acid must be applied. When sulphuric acid has been used in mordanting, it is often beneficial to add about 5 per cent. sodium acetate to the ultimate dye-bath to neutralise the mineral acid which always remains in the wool fibre (and which otherwise would be converted into potassium sulphate if tartar had been employed). The mordanting bath is prepared with the necessary quantities of aluminium sulphate and tartar (or its substitutes), and the wool is entered at a low temperature. During one to one and a-half hours the bath is heated gradually to boiling, and boiled for half an hour more. When the bath has cooled down the wool is taken out and thoroughly washed in water; boiling out with water is beneficial. It has been shown that washing is absolutely necessary to remove all loosely adhering mordants and to prevent rubbing of the ultimate colour. The washing, moreover, removes some of the acid, which is absorbed by the wool, and would be injurious in dyeing.

The washed wool is ready for dyeing; it should not be allowed to dry, as it is then very difficult to wet out again.

Application to Silk.—The theory of the mordanting of silk with primary metallic mordants—*e.g.*, by the unassisted action of metallic mordants—due to the affinity of fibre to mordant has been very thoroughly investigated by a long series of experiments by P. Heermann. He leans to the theory that the fibre acts catalytically, but considers that when the electro-chemical theories shall have become more developed, a more satisfactory explanation will be found in them.*

Silk dyers do not often use aluminium mordants; in the first place, they employ chiefly direct colours—*i.e.*, colours that do not require mordants—and in addition the alumina causes the fibre to lose some of its lustre and pliability.

The mordanting takes place at, or a little above, the ordinary temperature, to prevent the silk from losing its gloss and feel by the action of the mordant; this makes it necessary to use aluminium salts which dissociate readily. In silk dyeing, alum has not been replaced yet by aluminium sulphate, probably owing to the circumstance that slightly basic alum decomposes more readily than basic sulphate on account of the ammonium or potassium sulphate present in the former. The basic alum-bath may be prepared in the following manner:

* *Journ. Soc. Dyers and Col.*, 1903-1906.

—10 parts of alum are dissolved together with 1 part of soda crystals in sufficient water for complete solution (about 150 parts), and the liquor is gently heated until the precipitate first formed has completely disappeared. For every 10 lbs. of alum ¾ oz. of tin crystals may be added. Aluminium sulphate-acetate and nitrate-acetate are used in a similar way. The silk is thoroughly wetted out, wrung evenly, and passed into the mordanting bath. It is turned a short time without heating and then allowed to soak in the liquid for 12 hours. After this it is wrung and washed in water or, preferably, passed first through a solution of silicate of soda (1° Tw.) to fix the alumina; instead of the silicate a soap-bath may be employed. The silk is finally washed in water to remove all excess of mordant and fixing agent, and is then ready for dyeing. It should not be allowed to dry after mordanting, since it is afterwards difficult to wet out again and acquires an unpleasant feel.

During the steeping process the silk absorbs basic sulphates or basic sulphate-acetates, or nitrate-acetates. By the subsequent treatment with water or silicate of soda or soap the basic salts are decomposed and aluminium hydroxide is precipitated in the fibre. On account of all solutions being used cold gelatinous hydroxide is formed, and this is less liable to exert an injurious effect on the silk than the more crystalline hydrate which is formed at higher temperatures.

The composition of the mordanting baths remains fairly constant, and they may be used continuously if they are freshened up each time.

The following method was recommended by H. Lange as giving very good results:—10 parts of alum and 4 parts of sodium thiosulphate are dissolved in 100 parts of water and the silk is treated in this solution for three hours, the bath being heated during the first hour to 40°, during the second hour to 60°, and during the third hour to 80° C.; the silk is then rinsed and dyed.

CHROMIUM, Cr = 52·1.

Chromium is a trivalent metal, the symbol and atomic weight of which are Cr. and 52·1 respectively. It is of no practical interest as a metal. The chief ore from which most of the chromium compounds are obtained is *chrome iron ore*, FeO, Cr_2O_3. Compounds of chromium are largely used, on account of their inherent colour, as pigments in painting and printing; they form, also, the chromogenous substance of chrome-yellow and chrome-orange in dyeing proper. As mordants they are of the highest value, and, finally, the bichromates are very important oxidising agents, both in the laboratory and in the arts—*e.g.*, in the manufacture of Alizarin.

The formulæ of the derivatives of chromic oxide, like those of the aluminium compounds, are usually written with two atoms of chromium—*e.g.*, $Cr_2(OH)_6$ instead of $Cr(OH)_3$, and Cr_2Cl_6 instead of $CrCl_3$, because it was also believed that chromium was quadrivalent and acted as a hexavalent double atom, $Cr_2^{VI.} = \equiv Cr - Cr \equiv$.

Chromium forms three different compounds with oxygen:—

1. Chromium monoxide, CrO.
2. Chromic oxide, Cr_2O_3.
3. Chromium trioxide, CrO_3.

Chromium monoxide has scientific interest only.

Chromic Oxide or Chromium Sesquioxide, Cr_2O_3.—Chromic oxide is formed as a green amorphous powder, or very dark green hexagonal crystals by heating chromic hydroxide or ammonium bichromate; it is not readily soluble in acids.

Chromic oxide is used as a green pigment under the name of chrome-green.

Chromic Hydroxide $Cr(OH)_3$ or $Cr_2(OH)_6$—*Chromic Hydrate; Chromium Hydroxide.*—Chromic hydroxide is obtained by the addition of ammonia to solutions of chromium salts—

$$Cr_2(SO_4)_3 + 6NH_3 + 6H_2O = 2Cr(OH)_3 + 3(NH_4)_2SO_4.$$

Caustic potash or soda and the alkaline carbonates act in the same manner; the carbonates form basic carbonate of chromium.

The normal colour of chromium hydroxide is green, and its composition is $Cr_2O_3 + 5H_2O$, or $Cr(OH)_3 + H_2O$.* The chromic hydrates precipitated by a quantity of alkali insufficient to precipitate the whole amount present are always of a green colour; if the reagent is in excess, the precipitate is violet-blue. A violet precipitate can be transformed into a green through the loss of water. On adding ammonia to cold solutions of chromium salts, a dark green gelatinous substance is formed, while in precipitating boiling solutions a light green powder is obtained which is very difficultly soluble in acetic, sulphurous, and other acids. By drying the precipitate at 100° C., it becomes greyish-black, and has the constant composition $Cr(OH)_3 + H_2O$, or $Cr_2O_3 + 5H_2O$.

Sugar, oxalic, citric, and tartaric acids more or less impede the precipitation, and sometimes redissolve the precipitates on standing, forming violet solutions. The precipitate partly dissolves in an excess of ammonia, with a pale violet colour; on boiling, the precipitation is complete. In caustic potash or soda the precipitate dissolves with an emerald-green colour, but is completely thrown down by continued boiling, the supernatant liquor becoming decolourised. According to A. Recoura † chromium hydroxide is gradually dehydrated by the action of caustic soda, and is finally converted into chromic oxide, insoluble in acids. The solution is also precipitated by ammonium chloride. The hydroxide is but sparingly soluble in solutions of the alkaline carbonates. When precipitated in the presence of a magnesium compound, chromium hydroxide, like aluminium hydroxide, does not redissolve readily (see p. 222).

Chromium hydroxide, on being heated to 200° C. in a current of hydrogen, is changed to the *hydroxide*, $CrO(OH)$, and, on further heating forms chromic oxide.

The fine pigment, *Guignet's green*, is the *chromium hydroxide*, $Cr_2O(OH)_4$, and is obtained by melting potassium bichromate with boracic acid. It is insoluble in water, and but slowly affected by boiling acids.

By dialysis of a solution of chromium hydroxide in chromium chloride a *soluble chromium hydroxide* is formed, which contains for 66 equivalents of $Cr(OH)_3$ 1 equivalent of HCl (*Graham*).

Chromic hydroxide strongly resembles aluminium hydroxide. It forms *chromium salts* with acids, but acts towards caustic potash and soda as a very weak acid, forming therewith salts which are called *chromites*.

Chromites.—Potassium- and sodium-chromite are obtained by dissolving chromic hydroxide in three equivalents of caustic lye—

$$Cr(OH)_3 + 3NaOH = Cr(ONa)_3 + 3H_2O.$$

The alkaline chromites have not been prepared in the solid state. The affinity of the alkalies for chromium hydroxide is weaker than that which they evince for aluminium hydroxide. All acids (even carbon dioxide) and ammonium salts decompose the solutions of alkaline chromites. Moreover, these solutions are slowly dissociated, if free from an excess of caustic alkali. If a

* Prudhomme, *Journ. Soc. Dyers and Col.*, 1890, p. 147.

† *Comptes rendus*, 1895, cxx., p. 1335.

textile fibre is present the decomposition is effected more rapidly, owing apparently to the fibre, &c., exercising a catalytic action. Boiling at once precipitates chromium hydrate. In all cases chromic hydroxide is precipitated which does not readily redissolve on adding an excess of caustic soda.

Chromic hydroxide in its alkaline solution has the curious property of dissolving other metallic oxides, such as the ferric and the cupric oxides. Ferric oxide dissolves readily, and the brown solution remains clear for weeks without any precipitate forming. The alkaline solution of chromic and cupric oxide is blue; on heating to incipient boiling, red cuprous oxide is precipitated and sodium chromate formed.

Sodium Chromite.—H. Koechlin's *Alkaline Chrome Mordant* (see p. 251).

Chromium- or Chromic Salts.—The salts in which chromium acts as a base have a green or a violet colour. Some of them dissolve in water, and most of them in hydrochloric acid; those which are soluble in water have a disagreeable astringent taste and an acid reaction (as shown by their reddening blue litmus). The solutions have a fine dark-green or dark-violet colour; on heating them to over 65° C. the latter colour passes into the former, but returns, sooner or later, on cooling. Only the violet solutions yield crystalline salts, whereas the green solutions deposit amorphous compounds when evaporated. The former contain normal salts, while the latter are believed to be mixtures of acid and basic salts. The behaviour of the chromium salts to carbon dioxide, sulphuretted hydrogen, and ammonium sulphide is like that of the aluminium salts. Their reactions with the alkalies have already been referred to in the description of the hydroxide. On the whole, the chromium salts are more stable than the aluminium salts, and for this reason they are not so easily fixed on the cotton fibre as the latter.

Liechti and Schwitzer* found that normal chromium salts are not dissociated either by heat or by dilution with water. The basic chromium salts are less easily decomposed than the corresponding aluminium compounds, but the more readily, the greater the basicity of the salt is. The quantity of chromium retained by the fibre during the consecutive processes of mordanting, drying, and ageing increases also with the basicity of the mordant; the strongly basic sulphates yield apparently the greatest quantity to the cotton fibre, but not as much as the aluminium mordants. The influence of other salts present in the mordanting solution appears doubtful in the light of Liechti and Schwitzer's experiments, which are somewhat discrepant. It seems, however, that such salts have an influence opposite to that which they exert on the aluminium salts—that is, they make the salts more stable. Freshly-prepared solutions of chromium salts resist dissociation more powerfully than those which have been kept for some time.

Chromium Sulphate, $Cr_2(SO_4)_3$.—This salt is obtained by dissolving chromium hydroxide in sulphuric acid; the solution, which is at first green, becomes blue after some weeks standing, and yields a crystalline greenish-blue mass. By repeated crystallisation from diluted alcohol, violet-blue regular octahedra ($Cr_2(SO_4)_3 + 15H_2O$) can be obtained. The ordinary solutions of chromium sulphate are either violet or green; the violet solutions become green when boiled. Barium chloride throws down all the sulphuric acid from the violet solutions at the ordinary temperature; but only by prolonged boiling from the green solutions. The solutions of chromium sulphate are precipitated on addition of caustic soda, ammonia, or the carbonates, phosphates, arsenates, and silicates of the alkalies. The precipitate dissolves in an excess of caustic soda, and in a great excess of ammonia, but is completely thrown down again on boiling.

Basic chromium sulphates may be prepared by dissolving chromium

* *Journ. Soc. Chem. Ind.*, 1885, p. 586.

hydroxide in the solutions of the normal sulphate, or of chrome-alum, or by the addition of sodium hydroxide, &c.

They are less liable to decomposition in the presence of sodium sulphate. The most basic salt that can be obtained by dissolving chromium hydroxide in chromium sulphate is that having the composition $Cr(SO_4)(OH)$; whereas, by neutralising with sodium carbonate, the salt, $Cr_4(SO_4)_3(OH)_6$, is formed, which decomposes spontaneously after standing for three months. From chrome-alum (*i.e.*, in the presence of other sulphates) a still more basic salt, $Cr_2SO_4(OH)_4$, can be prepared with sodium carbonate, but not with chromium hydroxide (see below).

Normal chromium sulphate is not decomposed either on heating or on diluting with water, nor by the combined action of heat and dilution. The basic salts in concentrated solutions are not dissociated by boiling, but they are by diluting with water and by dilution and heat acting together. The more basic they are the more readily they are decomposed. The exact data as to dissociation can be seen from the table given in connection with chrome-alum.

Chromium sulphate is not used in the pure state, but, as chrome-alum, it is employed in the preparation of other chromium compounds.

Chrome Alum, $Cr_2K_2(SO_4)_4 . 24H_2O$.—This salt is obtained in great quantities as a bye-product in the manufacture of Alizarin, in which case it contains, notwithstanding its beautiful crystallisation, a considerable amount of impurities, including calcium sulphate, tarry organic matter, and free sulphuric acid. The pure salt may be prepared by reducing potassium bichromate by means of starch, sugar, glycerin, alcohol, oxalic or sulphurous acid, or other reducing agents; the requisite amount of sulphuric acid must be added. The reaction is explained by the equation—

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2 = Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O.$$

When sulphur dioxide is used, the reaction is as follows:—

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = Cr_2(SO_4)_3 + K_2SO_4 + H_2O.$$

For the preparation of pure chrome-alum dissolve

2 kgs. (2 lbs.) potassium bichromate in
10 litres (1 gall.) water, add
3 kgs. (3 lbs.) sulphuric acid,

heat to 35° C., and add alcohol slowly, until a pure dark-green colour is obtained. The double salt, $Cr_2K_2(SO_4)_4 + 24H_2O$, is obtained from the liquor by crystallisation.

Chrome-alum crystallises in large dark-violet octahedra, which dissolve with a violet colour in cold water. The solution becomes green on being heated to above 65° C. Chrome-alum is very soluble in water; 1 part of the salt dissolves in 7 parts of cold and in 2 parts of hot water. It is insoluble in absolute alcohol.

Chrome-alum contains 39·3 per cent. of $Cr_2(SO_4)_3$ = 15·3 per cent. of Cr_2O_3. The equivalent of the salt may, for all practical purposes, be considered to be 1,000 instead of 998·9.

The behaviour of chrome-alum towards barium chloride is like that of chromium sulphate. The basic salts obtained from chrome-alum are less prone to dissociation than those prepared from the pure sulphate. The results obtained by Liechti and Schwitzer in their study of the dissociation of chromium sulphates are stated in the following table. They worked with solutions equivalent to 225 grms. of crystallised chrome-alum per litre (*i.e.*, equivalent to 150 grms. of crystallised aluminium sulphate).

Cotton was mordanted with the solutions, and aged; the fifth column in the table shows the percentage of chromic oxide fixed thereby, calculated on the amount offered to the fibre by impregnating. The first column gives the composition of the sulphate; the second the mode of its preparation (from which the amount of potassium or sodium sulphate present can be seen); the third column states the relative dilution which effects dissociation; while the fourth shows the degree of the dilution by which the salts are decomposed on boiling. As stated before, the normal or basic chromium sulphates are not dissociated (by boiling) in a solution of the indicated strength, either in the presence or absence of alkaline sulphates.

Table showing the dissociation of Chromium Salts in a solution equivalent to 225 grms. of crystallised Chrome-alum per litre.

Composition.	Origin of Salt.	Dissociated by Cold Dilution.	Dissociated by Boiling Dilution.	Per Cent. Cr_2O_3 retained by the Cotton Fibre.
1. $Cr_2(SO_4)_3$.	Pure sulphate.	Not dissociated.	Not dissociated.	12 8 per cent.
2. $Cr_2(SO_4)_3$.	Chrome alum.	Do.,	Do.,	1·8 „
3. $Cr(SO_4)(OH)$.	Pure sulphate and $Cr(OH)_3$.	10 fold.	0 5 fold.	28·0 „
4. $Cr(SO_4)(OH)$.	Pure sulphate and Na_2CO_3.	6·5 „	2 „	39·0 „
5. $Cr(SO_4)(OH)$.	Chrome-alum and $Cr(OH)_3$.	85 „	10·5 „	29·7 „
6. $Cr(SO_4)(OH)$.	Chrome-alum and Na_2CO_3.	85 „	12 „	7·6 „
7. $Cr_4(SO_4)_3(OH)_6$.	Pure sulphate and Na_2CO_3.	1·25 „	0·4 „	86·4 „
8. $Cr_4(SO_4)_3(OH)_6$.	Chrome-alum and $Cr(OH)_3$.	2 „	0·25 „	43·0 „
9. $Cr_4(SO_4)_3(OH)_6$.	Chrome-alum and Na_2CO_3.	16 „	2·6 „	22·6 „
10. $Cr_2(SO_4)(OH)_4$.	Chrome-alum and Na_2CO_3.	1·5 „	0·5 „	87·5 „

On the whole, this table shows that a basic sulphate becomes more stable in solution with increasing amounts of alkaline sulphates, whereas, with increase of basicity the sensitiveness of the sulphate towards dissociation becomes greater.

Chrome-alum is chiefly used for the preparation of other chromium compounds, and finds application for the fixing of direct cotton colours.

Chromium Chloride, $CrCl_3$ or Cr_2Cl_6—*Chromic Chloride.*—Chromic chloride in the pure state is obtained as a sublimate, in beautiful violet crystals, by passing a current of chlorine gas over a red-hot mixture of chromic oxide and charcoal. These crystals do not dissolve readily in water unless a trace of chromium dichloride, $CrCl_2$, be present. The solution yields green crystals of the composition $CrCl_3 + 6H_2O$, which are deliquescent in the air. By drying in the desiccator they form basic or oxychlorides, $CrCl_2OH$ and $CrCl(OH)_2$, and finally hydroxide, $Cr(OH)_3$. On evaporating to dryness, the solution gives rise to hydrochloric acid and basic chlorides.

The commercial article is obtained by the double decomposition of chrome-alum or chromium sulphate with calcium chloride, or by dissolving chromium hydrate in hydrochloric acid, and is sold as a dark-green solution. Another method of preparing chromium chloride is to heat bichromate, hydrochloric

acid, and treacle or molasses in suitable proportions. It is doubtful whether a pure chloride is thus formed; the product probably contains some organic acid.

Basic chromic chloride, $CrCl(OH)_2$, has been introduced by the Badische Anilin- und Soda-Fabrik as a mordant for cotton and silk. It is prepared by saturating a solution of chromic chloride with chromic hydroxide, or by using an excess of hydroxide and filtering. The mordant is used on cotton and silk like the basic aluminium sulphates.

Chromium Fluoride, $CrF_3 + 4H_2O$.—This salt was introduced in 1888 by G. Stein. It comes into the market in the form of a green crystalline powder, which corresponds to 42 per cent. of chromic oxide, Cr_2O_3. The normal salt seems to be stable in aqueous solutions, and not to be dissociated by heating or diluting. It is very soluble in cold and hot water, and forms a green solution. Since it has a corroding action on glass and on most metals, it must be kept in wooden vessels, and leaden tubes should be used as steam pipes. Working in copper vessels is said, however, to be without serious disadvantages. Additions of small quantities of chromic acid, chromates, or hydrogen peroxide to the mordanting bath protect the copper against the action of hydrofluoric acid. The best protection, however, is, according to A. Kertess, to place some strips of zinc into the bath, the copper not being attacked as long as some zinc is present. Basic chromium fluorides (oxyfluorides) decompose on being evaporated, chromium hydroxide being separated. Chromium fluoride has been recommended as a mordant both for vegetable and animal fibres.* The value depends upon the non-injurious action of the liberated hydrofluoric acid upon fibres and colours. It is claimed that this salt can replace bichromate with advantage in wool dyeing, where the oxidising action of the latter is injurious—*e.g.*, for chroming indigo-dyed wool. In cotton dyeing, it is used for fixing certain direct cotton colours fast to washing, such as Diamine fast red F, Diamine green G, and Diamine brown M. A mordanting bath of chromium fluoride can be used continuously.

Chromium Nitrate, $Cr(NO_3)_3$ or $Cr_2(NO_3)_6$, is prepared by dissolving chromic hydroxide in nitric acid, or by the double decomposition of chrome-alum and lead acetate. By reducing bichromate in the presence of nitric instead of sulphuric acid, chromium nitrate is also produced. The salt crystallises with 9 molecules of water of crystallisation in purplish-red crystals, but these crystals are not easily obtained, as the solution generally yields an amorphous green mass. The article is sold as a blue solution, which appears red by transmitted light; it is not extensively used. Basic salts are obtained from the solution by means of chromic hydroxide, soda, &c. Chromium nitrates behave in the same way as the corresponding sulphates and chlorides. Of the three kinds of salts, the sulphates seem to be the most stable, next come the chlorides, and then the nitrates, the last being the most readily dissociated.

Chromium nitrates, normal and basic, serve as mordants for cotton. In former years they were employed to produce a light green shade on calico. The pieces were simply impregnated with the solution, and aged when the green colour of chromium hydroxide appeared (*Schuetzenberger*).

Chromium Chlorate, $Cr(ClO_3)_3$ or $Cr_2(ClO_3)_6$.—This salt may be prepared by the double decomposition of chrome-alum and barium chlorate. Its solution is violet or green, according to the temperature at which it has been prepared. A certain amount of barium sulphate always remains in solution, but is precipitated by boiling the solution or by adding hydrochloric acid.

Chlorate of chromium evolves a distinct odour of chlorine, and when heated to 100° C. it gives off large quantities of chlorine, and becomes

* G. Stein, *Journ. Soc. Dyers and Col.*, 1888, p. 60. H. Lange, *Journ. Soc. Dyers and Col.*, 1888, p. 73; 1891, p. 121.

transformed into a yellowish-red liquid containing chromic acid and oxygen compounds of chlorine. The solution decomposes after a few days.

Chromium chlorate is a powerful oxidising agent. Prudhomme, who describes this salt (*l.c.*), has advantageously used a boiling solution of it for the purpose of making Aniline black ungreenable.

Basic chromium chlorate is used in calico-printing to produce steam Catechu brown (*oxidation-mordant*).

Chromium Bisulphite, $Cr(HSO_3)_3$ (?).—If a current of sulphur dioxide is passed through water in which chromium hydroxide (cold precipitated) is suspended, a yellowish-green solution is obtained, which probably consists of chromium bisulphite—$Cr(OH)_3 + 3H_2SO_3 = Cr(HSO_3)_3 + 3H_2O$. The same compound is formed when a solution of a chromium salt is mixed with a bisulphite—$Cr_2(SO_4)_3 + 6NaHSO_3 = 2Cr(HSO_3)_3 + 3Na_2SO_4$. For the preparation of the substance a very strong solution of chrome-alum may be mixed with strong liquor of bisulphite of soda, until the bluish-green colour has changed to yellowish-green; an excess of bisulphite is advantageous. After a few days Glauber's salt crystallises from the mixture. The solution, however, can be used immediately after being prepared.

Chromium bisulphite in solution yields on boiling a green precipitate which appears to be normal chromium sulphite, $Cr_2(SO_3)_3$, or a basic salt. Geuther gives it the formula $Cr_4S_3O_{12} + 16H_2O$.

Prudhomme* states that the solution of chromium hydrate in sodium bisulphite liquor deposits after some time a green powder of chromium sulphite.

Chromium bisulphite decomposes on the fibre by steaming or drying, leaving chromium hydroxide; so that it is well adapted for mordanting cotton piece goods.

The pieces are padded in the solution, rolled up for two hours, and passed through Mather & Platt's steamer (see *Aniline black*). Before padding, the goods may be oiled. Instead of steaming they may be simply dried; but in this case they are very difficult to wet. After drying or steaming they are well washed in water, or in soda, if it is desirable to remove with certainty all sulphur dioxide from the fibre.†

Chromium Sulphocyanide or Thiocyanate, $Cr(CNS)_3$ or $Cr_2(CNS)_6$.—By dissolving chromium hydroxide in hydrosulphocyanic acid a green-violet solution is obtained, which yields a dark-green amorphous and deliquescent salt of the composition, $Cr(CNS)_3$. The commercial article is prepared by the double decomposition of chrome-alum or chromium sulphate with barium or calcium sulphocyanide.

Basic sulphocyanides are obtained by adding chromium hydroxide, soda, &c., to the normal salt. They possess great stability; the most basic salt, $Cr_2(CNS)(OH)_5$, however, decomposes after some hours standing. Chromium sulphocyanide forms crystalline double salts with other sulphocyanides—*e.g.*, potassium-chromium sulphocyanide, $Cr(CNS)_3 + 3K(CNS) + 4H_2O$.

Solutions of the sulphocyanides do not dissociate either on heating or on diluting with water, except in the case of very dilute solutions of the more basic salts, which are decomposed on heating.

Sulphocyanides of chromium yield but small quantities of chromium to the cotton fibre by the operations of mordanting, drying, and ageing. Comparison with chrome-alum shows, according to Liechti and Schwitzer, that this is a much better cotton mordant than the sulphocyanide.‡

* *Journ. Soc. Dyers and Col.*, 1890, p. 148.

† E. Kur, *Journ. Soc. Dyers and Col.*, 1890, p. 70.

‡ Lauber (*Handbuch des Zeugdrucks*) states, on the contrary, that chromium sulphocyanide in print colours gives off the chromium with great ease and is an excellent mordant.

Sulphocyanide of chromium is used by calico-printers for the production of steam logwood blacks. It behaves in the same way as the corresponding aluminium salt towards the fibre, not injuring the same.

Chromium Phosphates.—Chromium hydroxide dissolves in solution of phosphoric acid with a green colour. Phosphate of soda precipitates normal chromium phosphate, $CrPO_4$, from solutions of chromium salts as a green mass, which becomes dark blue on drying.

Chromium Arsenite was formerly produced on the fibre as a self-colour of a light green shade; cotton piece goods were padded with a chromium salt and passed through a solution of arsenite of soda.

Chromium Acetate, $Cr(C_2H_3O_2)_3$ or $Cr_2(C_2H_3O_2)_6$.—Normal chromium acetate is prepared by dissolving chromium hydroxide in the requisite amount of acetic acid; or by the double decomposition of chrome-alum or chromium sulphate and lead acetate or calcium acetate. The salt has been obtained as hexagonal tablets, having the composition $Cr(C_2H_3O_2)_3 + H_2O$. The solution of chromium acetate is violet, and becomes greenish on being heated. It is not at all subject to dissociation; the salt can be evaporated to dryness and even heated without losing its solubility. The violet and green solutions of chromium acetate differ greatly in stability. The solutions are not readily precipitated at the ordinary temperature on addition of caustic alkalies, alkaline carbonates, phosphates and silicates, ammoniacal soap, or Turkey-red oil; but complete precipitation takes place on boiling the solutions with these additions for a longer or shorter period according to the degree of dilution; very long continued boiling is necessary if phosphate of soda is the precipitating agent.

It is usually prepared by one of two methods:—

(1) *From Chrome Alum.*—Add soda to a solution of the chrome alum, until the desired basicity is obtained, evaporate down to point of crystallisation to let sodium and potassium sulphate separate out. Then dilute somewhat and add the necessary amount of calcium acetate. Filter and evaporate down to 32° Tw. or to dryness.

(2) *From Sodium Bichromate.*—Add sulphuric acid in sufficient amount to liberate chromium trioxide, then acetic acid (pyroligneous) and glucose. A violent reaction takes place which results in the reduction of CrO_3 to $Cr(OH)_3$ and this dissolves in *statu nascendi* in the acetic acid. This solution probably contains other compounds besides the acetate.

Basic chromium acetates are prepared from the normal salt by the addition of chromium hydroxide, ammonia, caustic or carbonate of soda, &c., or by adding lead acetate or calcium acetate to basic sulphates. The violet solutions retain their violet colour on addition of basic agents, while the most basic salts prepared from violet solutions are less sensitive to dissociation than the compounds similarly prepared from green solutions. This is in accordance with the supposition that the green solutions consist of mixtures of acid and basic salts; an addition of caustic soda, for example, would produce a more basic salt in a green solution than in a violet. Liechti and Schwitzer examined the chromium acetates for their dissociating and mordanting properties. They used solutions equivalent to 225 grms. chrome-alum per litre, which were prepared from normal sulphate or basic sulphate and lead acetate. Only the most basic salts were dissociated by heat alone. The normal salt and the first basic salt, $Cr_2(C_2H_3O_2)_5(OH)$, could not be decomposed by boiling, and the second basic salt, $Cr_2(C_2H_3O_2)_4(OH)_2$, only by the combined action of a seventy-five-fold dilution and boiling. None of the salts were dissociated by simple dilution with water. On mordanting, drying, and ageing the cotton fibre retained of the available chromium

From the normal salt,	$Cr_2(C_2H_3O_2)_6$	: 8·4 per cent.
,, basic ,,	$Cr_2(C_2H_3O_2)_5(OH)$	: 25·7 ,,
,, ,, ,,	$Cr_2(C_2H_3O_2)_4(OH)_2$	: 30·0 ,,
,, ,, ,,	$Cr_2(C_2H_3O_2)_3(OH)_3$	: 66·0 ,,
,, ,, ,,	$Cr_2(C_2H_3O_2)_2(OH)_4$	: 69·9 ,,

Solutions of more basic acetates than these can be prepared. Chromium acetate (and chromium nitrate-acetate also) is not readily precipitated by sodium carbonate; only on heating, a precipitate is obtained; a cold solution of chromium acetate remains clear even when three equivalents of sodium carbonate (Na_2CO_3) are added for 2 equivalents of $Cr(C_2H_3O_2)_3$. Chromium acetates will dissolve lead sulphate in quantities increasing with the basicity of the chromium acetate; thus the addition of acetic acid to a basic salt precipitates the sulphate.

The great stability of chromium acetate somewhat prevents its application in cotton dyeing, while it is not used at all in wool or silk dyeing. It is, however, the most important chromium mordant for printing on cotton and woollen goods; the normal salt is employed. To prepare chromium acetate precipitate 1,000 parts of chrome-alum with 330 parts of soda ash (58°), filter, wash and press the precipitate, and dissolve it in 1,300 parts of acetic acid (30 per cent.). The solution may be concentrated by boiling; the usual strength is 32° Tw.

Chromium Sulphate-Acetates.—These salts are prepared, analogously to the corresponding aluminium salts, by decomposing chromium sulphate with an amount of lead acetate insufficient to effect complete decomposition, or by the addition of sodium acetate. By decomposing basic sulphates basic sulphate-acetates are obtained. In their general behaviour they resemble the chromium sulphates. Liechti and Schwitzer state that of the chromium sulphate-acetates, neither the normal nor the basic is decomposed by dilution with water. The more basic salts only are dissociated by heat. The salt, $Cr_4(SO_4)(C_2H_3O_2)_4(OH)_6$, yields on mordanting, drying, and ageing 84 per cent. of the available chromium to the cotton fibre.

Chromium Chloride-Acetates are obtained by dissolving chromium oxychloride (basic chloride) in acetic acid, or by acting on a solution of chrome-alum with calcium chloride and calcium-acetate. The most basic salts only show signs of dissociation by the combined action of heat and dilution. The salt, $Cr_2Cl(C_2H_3O_2)_2(OH)_3$, yields to the cotton fibre on mordanting, &c., 50 per cent. of its chromium (*Liechti and Schwitzer*).

Chromium Nitrate-Acetates.—By evaporating a solution containing 5 equivalents of normal chromium acetate and 1 equivalent of normal chromium-nitrate, a salt is obtained which crystallises in green tablets, having the composition $Cr_2(NO_3)(C_2H_3O_2)_4(OH)$. By recrystallising this salt from strong acetic acid the salt $Cr_2(NO_3)(C_2H_3O_2)_5$ is formed.

Chromium nitrate-acetates are prepared by double decomposition of the sulphates with lead nitrate and lead-acetate. Another method, which is recommended by Witz,* is to reduce potassium bichromate with glycerin in the presence of nitric and acetic acids. The salt, $Cr_2(NO_3)(C_2H_3O_2)_2(OH)_3$, is thus obtained, according to the equation—

$$K_2Cr_2O_7 + 3HNO_3 + 2C_2H_4O_2 + 3H_2 = Cr_2(NO_3)(C_2H_3O_2)_2(OH)_3 + 2KNO_3 + 4H_2O.$$

3 kgs. (30 lbs.) crushed potassium bichromate,
4·4 litres (4½ galls.) boiling water, and
26 litres (26 galls.) nitric acid (66° Tw.)

are placed in an earthenware vessel standing in the open air; into this mixture are poured carefully

* A. Renard, "Traité des Matières Colorantes," *Journ. Soc. Dyers and Col.*, 1885, p. 61.

0·72 litre (3 quarts) white glycerin (48° Tw.), and
4 litres (4 galls.) acetic acid (30 per cent.),

half a litre (or 1 pint) at a time, constantly stirring with a long glass rod. When all the bichromate has dissolved, the mixture is rapidly brought to the boil in a copper boiler until a thin layer of the liquid appears of a fine green colour (about two minutes). An abundant crystallisation of saltpetre is obtained on cooling. The crystals are washed with water, and the washings added to the green liquor. About 12·6 kgs. (126 lbs.) (50° Tw.) are obtained.

Chromium nitrate-acetates may also be prepared by simply mixing chromium nitrate and chromium-acetate in the requisite proportions. Basic salts are obtained by adding sodium carbonate or by mixing basic salts.

Of the chromium nitrate-acetates the most basic only are dissociated by heat and by dilution. The salt, $Cr_2(NO_3)(C_2H_3O_2)_2(OH)_3$, is decomposed by the action of heat on a very weak solution, and yields to the cotton fibre 48·5 per cent. of its chromium. The salt, $Cr_2(NO_3)(C_2H_3O_2)(OH)_4$, is decomposed by heat alone, and deposits in the fibre by mordanting 69·1 per cent. of its chromium (*Liechti* and *Schwitzer*).

The chromium nitrate-acetates are employed as mordants in calico-printing.

Chromium Trioxide or Chromic Anhydride, CrO_3.—Chromium trioxide is obtained in the form of long ruby-red acicular crystals by adding an excess of strong sulphuric acid to a concentrated solution of the bichromate—

$$K_2Cr_2O_7 + H_2SO_4 = 2CrO_3 + K_2SO_4 + H_2O.$$

The crystals are very soluble in water, with which they form a solution of chromic acid (H_2CrO_4). Chromic acid is very easily reduced to chromic oxide by reducing agents like sulphur dioxide, sulphuretted hydrogen, arsenic, and many organic substances; the reaction is so vehement that ignition sometimes occurs, as is, for instance, the case when alcohol is brought in contact with the dry crystals. Heated with nitric or sulphuric acids, chromium trioxide forms chromium salts and nascent oxygen; in the case of hydrochloric acid, chlorine is generated—$2CrO_3 + 12HCl = 2CrCl_3 + 3Cl_2 + 6H_2O$. CrO_3, frequently used in the laboratory, is one of the most powerful oxidisers known.

In acid solutions the chromates are reduced in the same way as chromic acid, though less rapidly, by the action of oxidisable substances, and yield chromium salts; the reduction of chromates in alkaline solutions does not take place rapidly. Sulphur dioxide and sulphites yield with chromium trioxide chromium sulphate—

$$2CrO_3 + 3SO_2 = Cr_2(SO_4)_3.$$
$$2CrO_3 + 3Na_2SO_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3Na_2SO_4 + 3H_2O.$$

Bichromate is reduced in the absence of H_2SO_4 as follows (Knecht)—

$$K_2Cr_2O_7 + 4SO_2 = Cr_2(SO_4)_3 + K_2SO_3.$$

Potassium Chromate, K_2CrO_4—*Neutral* or *Yellow Potassium Chromate, Chromate of Potash.*—Potassium chromate is obtained by neutralising potassium bichromate with potassium hydroxide or carbonate. It forms yellow rhombic pyramids, which dissolve readily in water with a yellow colour, which is perceptible even in weak solutions. 100 parts of water dissolve about 60 parts of the salt at the ordinary, and less than 80 parts at the boiling, temperature.

Potassium chromate is readily converted by the action of acids into the bichromate. It is sometimes used in place of the bichromate.

Potassium Bichromate, $K_2Cr_2O_7$—*Red Chromate* or *Bichromate of Potash; Bichrome* or *Chrome.*—Potassium bichromate is manufactured by heating chrome iron ore with lime and potash, when the chromium oxide is oxidised by the atmospheric oxygen, and chromates of calcium and potassium are formed.

Potassium bichromate crystallises in large orange triclinic prisms or tables, which are stable in the air and contain no water of crystallisation (in contrast with the sodium salt); it melts below red heat, and at higher temperatures it decomposes, forming oxygen, chromium oxide, and normal chromate. Its solubility in 100 parts of water is at—

0° C.	10° C.	40° C.	80° C.	100° C.
Parts. 5	Parts. 8·5	Parts. 29·2	Parts. 73	Parts. 102

Potassium bichromate has a cooling, bitter, and metallic taste. It is poisonous, a property common to chromic acid and the chromates generally. Its dust is very harmful to the skin, and causes painful sores, which, according to H. S. Riederer,* may be healed by repeated treatments with a 5 per cent. solution of sodium bisulphite. The action of reducing agents on bichromate of potash has already been noticed.

Potassium bichromate, in presence of certain organic bodies, is affected in some way by the active rays of light. If a solution of the salt in gelatine is exposed to daylight, it becomes insoluble in water; those parts, however, which have not been so exposed remain soluble. This property is utilised in photography. The yellow colour of wool which has been mordanted with bichromate changes to green under the action of light, so that if the wool has not been completely exposed uneven dyeing will ensue. Judging from the green colour, a reduction of the chromic acid to chromic oxide has taken place.

Commercial potassium bichromate is almost chemically pure. It has now been replaced almost entirely by sodium bichromate, and both are the raw material for the production of all other chromium compounds and are used in various industries—*e.g.*, in the manufacture of Alizarin and the Chrome colours (Chrome-yellow, Chrome-orange, Guignet's green). Dyers use these bichromates very extensively. They are the most important wool mordants, while in cotton dyeing they are used in the production of Aniline black, Cutch brown, Chrome-yellow, for the after treatment of direct dyes, &c.

Sodium Bichromate, $Na_2Cr_2O_7 + 2H_2O$.—This salt strongly resembles bichromate of potassium, except that it contains 2 molecules of water of crystallisation, is deliquescent, and is very easily soluble in water. It is, however, much cheaper than the potassium salt, and is produced in an analogous way. The commercial product is sold (1) in cyrstals containing 2 molecules = 12 per cent. of water of crystallisation, or (2) in lumps or as a powder of the fused and partially dehydrated compound.

Sodium bichromate crystallises in prisms or plates of the triclinic system which are of a yellowish-red colour, transparent and deliquescent. It has an acid reaction, and a bitter, cooling, metallic taste. It loses 1 equivalent of water below 75° C., while all the water is given off below 100° C., leaving the anhydrous salt as a light brown mass. It decomposes slightly above its melting point (320° C.), giving off oxygen; hence the fused products always contain some chromic oxide. When the crystals of the hydrated salt are dissolved in water a considerable reduction of temperature occurs, while, if the anhydrous be treated with water, a rise in temperature is produced.

Arthur Stanley has published the following tables † of the solubility of anhydrous sodium bichromate in water and of the specific gravities of different aqueous solutions.

* *Journ. Soc. Chem. Ind.*, 1907, p. 511. † *Journ. Soc. Dyers and Col.*, 1886, p. 143.

100 parts of water dissolve of sodium bichromate ($Na_2Cr_2O_7$) at —

0° C.	15° C.	30° C.	80° C.	100° C.	139° C.
Parts. 107	Parts. 109	Parts. 127	Parts. 143	Parts. 163	Parts. 210

The specific gravities of solutions of different strengths are the following:—

Per Cent. $Na_2Cr_2O_7$.	Specific Gravity.	Per Cent. $Na_2Cr_2O_7$.	Specific Gravity.	Per Cent. $Na_2Cr_2O_7$.	Specific Gravity.	Per Cent. $Na_2Cr_2O_7$.	Specific Gravity.	Per Cent. $Na_2Cr_2O_7$.	Specific Gravity.
1	1·007	11	1·078	21	1·147	31	1·216	41	1·287
2	1·014	12	1·085	22	1·153	32	1·224	42	1·294
3	1·021	13	1·092	23	1·159	33	1·231	43	1·300
4	1·028	14	1·099	24	1·165	34	1·238	44	1·307
5	1·035	15	1·105	25	1·171	35	1·245	45	1·313
6	1·042	16	1·113	26	1·178	36	1·252	46	1·319
7	1·049	17	1·120	27	1·185	37	1·259	47	1·325
8	1·057	18	1·127	28	1·193	38	1·266	48	1·330
9	1·064	19	1·134	29	1·201	39	1·273	49	1·336
10	1·071	20	1·141	30	1·208	40	1·280	50	1·343

Sodium bichromate in the form of crystals with 2 molecules of water is nearly equivalent to the (anhydrous) potassium bichromate, the molecular weights of these two salts being in round numbers 299 and 295 respectively; the equivalent of the anhydrous sodium salt is 263.

Sodium bichromate is now generally used in place of potassium bichromate on account of its lower price and its greater solubility.

Lead Chromate ($PbCrO_4$) or *Chrome-yellow;* and **Basic Lead Chromate** (Pb_2CrO_5) or *Chrome-orange* (see *Mineral colours*).

Copper Chromates.—By the action of a concentrated solution of chromic acid on cupric hydroxide brownish-black deliquescent crystals of $CuCr_2O_7 + 2H_2O$ are obtained. When the solution of this salt is boiled the basic salt, $Cu_3CrO_6 + 2H_2O$, separates out as a brown precipitate. The latter is also obtained by mixing boiling solutions of normal potassium chromate and blue vitriol, whereas cold solutions form the double salt, $K_2CrO_4 + Cu_3Cr_2O_9 + 2H_2O$.

Mixtures of potassium bichromate and copper sulphate are employed with good results for mordanting wool, and after treating direct cotton colours, the copper sulphate increasing the fastness of the colour.

Chromium Chromate, $Cr_2(CrO_4)_3$ (?).—By dissolving chromium hydroxide in chromic acid, and carefully evaporating and crystallising several times, needle-shaped crystals of a salt are obtained, which have the composition, $Cr_2(CrO_4)_3 + 9H_2O$.* Whether the same product is obtained by the double decomposition of chromium sulphate and chromate of potassium is not certain.

Basic Chromium Chromate, $Cr_2(CrO_4)_2(OH)_2$, may also be prepared by the action of chromic acid on chromium hydroxide. It dissociates rapidly in solution.

Basic Chromium Sulphate-Chromate, $Cr_2(SO_4)(CrO_4)(OH)_2$, is obtained by dissolving 2 equivalents of chromium hydroxide, $Cr(OH)_3$, in 1 equivalent of sulphuric acid and 1 equivalent of chromic acid—

$$2Cr(OH)_3 + H_2SO_4 + H_2CrO_4 = Cr_2(SO_4)(CrO_4)(OH)_2 + 4H_2O.$$

* M. v. Gallois—German Patent, 45,999; English Patent, 1889, No. 376—*Journ. Soc. Dyers and Col.*, 1889, p. 30.

The same compound is formed by double decomposition when 2 equivalents of $Cr(OH)_3$ are dissolved in 2 equivalents of H_2SO_4, and the product is acted upon by 1 equivalent of the normal chromate, or ½ equivalent of bichromate of potassium or sodium.

The normal chromium chromate and the basic chromium sulphate-chromate are stable compounds in strong solutions. By boiling or by dilution with water they are dissociated, and the chromium hydroxide is precipitated in an insoluble form. The same effect is obtained by subjecting the salts in the fibre to the action of steaming, and by simply washing the fibre.

Under the name of chromium-mordants, G.A. I., G.A. II., and G.A. III., certain products are brought into the market by the Farbwerke, vorm. Meister Lucius & Brüning, which consist of chromium chromate or similar products.

Application of the Compounds of Chromium to the Textile Fibres as Mordants.

The salts of chromic acid are frequently employed in dyeing and printing. Chromic acid in the form of chromates or bichromates is also very extensively used as a mordant proper. It is, however, invariably the lower oxide of chromium—chromic oxide—which serves as the actual fixing agent, for, wherever chromic acid is employed as a mordant, it is reduced to chromic oxide before it forms the ultimate colour lake, either in the mordanting or in the dyeing process, or between these two in a separate operation. In other cases the goods are treated with bichromate after the dyeing, and then chromic acid acts as an oxidising agent, and chromic oxide, which is generated thereby, takes the part of a mordant. The behaviour of chromic acid on "chromed wool" towards oxidisable dyestuffs (such as logwood) is similar.

As the chromium salts and chromates are inseparable as mordants, they are here described together. The applications of chromic acid as an oxidising agent and as a dyestuff will be found in connection with the subjects where it acts as such (for instance, in the paragraphs on Aniline-black and Chrome-yellow).

Application to Cotton and Linen—(1) *Chromium Hydroxide in Alkaline Solution (H. Koechlin's Alkaline Chrome Mordant or Chromite of Soda).**— Koechlin mixes 2 measures of chromium acetate (25° Tw.) with 2 measures of caustic soda (66° Tw.) and ½ to 1 measure of water, then 1 measure of caustic soda lye in addition may be added to 5 measures of this mixture. If in the beginning only 1½ measures caustic soda instead of 2 are used, the liquor becomes muddy and gelatinous.

Chromium acetate is obtained by precipitating 1,000 parts of chrome-alum with 330 parts of soda ash (58°), washing the precipitate and dissolving it in acetic acid; the liquid is concentrated by boiling. H. Schmid † saves the expense of acetic acid by dissolving the precipitate of chromic hydroxide, obtained from 1,000 parts chrome-alum and 330 parts soda ash, in 50 parts (by weight) of caustic soda lye (50° Tw.). This alkaline mordant is not a stable product; after one or two days complete precipitation takes place; glycerin may delay this, but is liable to diminish the mordanting power. As the bath remains clear in the presence of a great excess of caustic soda, a known quantity of the latter is added to preserve the liquor, and this is neutralised with a corresponding amount of chromic hydroxide before the bath is used again. In all cases, however, only the requisite quantity of mordant should be prepared. The more caustic the bath the better it mordants; if insufficient soda is present, very little chromic hydroxide will precipitate,

* *Journ. Soc. Dyers and Col.*, 1885, p. 18, and 1886, p. 25. † *Ibid.*, 1886, p. 26.

notwithstanding complete solution. On the other hand, too great causticity shrinks the fibre seriously by the action of mercerising.

A simplified method is the following:—

200 grms (2 lbs.) chrome-alum,
1 litre (1 gall.) water, and
½ litre (½ gall.) caustic soda (71° Tw.)

are mixed; the pieces are passed through this solution, beamed, and left for 24 hours, then passed through boiling water, washed, and dyed.*

Koechlin's alkaline mordant is one of the best chromium mordants for cotton which has been proposed. Unfortunately, it cannot well be used for yarns, on account of its caustic action on the hands of the workmen. Another disadvantage is that it cannot be used on oiled material, since the oil would be stripped from the fibre. Cotton piece goods are saturated with the cold liquor on the padding machine, rolled up and left for twelve hours, then washed, if possible, in running water. This mordanting process is not at all analogous to the fixation of alumina by means of aluminate of soda. The precipitation takes place by mere contact, and fixing agents are useless.

(2) *Chromium Salts as Mordants.*—It is difficult to impregnate the vegetable fibres with an amount of chromium salt sufficient to obtain a full shade. The sulphates, nitrates, acetates, nitrate-acetates, &c., have been employed with good results in calico-printing, but the demand for a good chromium mordant for the dyeing of cotton, especially of cotton yarns, has not been completely satisfied as yet.

Horace Koechlin has proposed the following method, which gives fairly good results:—The yarn is impregnated with the solution of a chromium salt, preferably a basic salt, dried and passed through a boiling solution of 1 part of soda ash in 10 parts of water; the operations are repeated if sufficient chromium has not been fixed. Chrome-alum, chromium sulphate, nitrate, chloride, acetate, nitrate-acetate, &c., or their basic salts (like $Cr_4(SO_4)_3(OH)_6$) are used; the acetates, and nitrate-acetates, yield less satisfactory results since they are not readily precipitated. It is essential that the soda solution be kept at the boiling temperature; since, otherwise, a smaller amount of the mordant will be fixed. Other salts, such as phosphate of soda, do not give such good results as sodium carbonate.

Better results are obtained if the fibre is prepared first with Turkey-red oil or tannin, or both, and subsequently with chromium salts. In this case the soda solution is replaced by cold water containing a small amount of lime, since soda would affect the organic mordant. The material is impregnated with 1 part of neutralised Turkey-red oil and 9 parts of water, or in the case of tannin being used, it is steeped in a bath containing 1 part of sumach extract (52° Tw.) in 100 parts of water. The goods are entered into the bath at boiling temperature, and allowed to soak twelve hours without further heating. Both processes may be combined by first oiling the goods and then preparing them with sumach. The material is simply wrung after these operations and passed into the chromium-mordant bath, where it is left for two to four hours; but when Turkey-red oil alone is used, it is better to leave the goods over night in the chrome-bath. After being wrung out the material is washed in water containing some lime, and is ready for dyeing. For full shades the various operations are repeated. The best mordant for this process is basic chromium chloride (32° Tw.); other easily decomposed chromium salts, such as the sulphate, acetate, or chromate, are also applicable.

The Badische Anilin- und Soda-Fabrik recommends the following treatment:—The cotton is steeped over night in a bath of basic chromium chloride,

* Private communication from M. Horace Koechlin.

32° Tw., and then wrung out and well washed in a flow of calcareous water. This first treatment is followed for medium shades by further mordanting with Turkey-red oil and chromium chloride, 32° Tw., and for dark ones with Turkey-red oil, sumach, and chromium chloride, as just described.

Chromium bisulphite is not suitable for the mordanting of yarns. Cotton piece goods are mordanted with this product in the padding-machine, and left to lie beamed for two hours; they are then dried, or, better, passed through the rapid ager of Mather & Platt, and washed in water; it is not advisable to dry the material, because it is afterwards difficult to wet out.

The following instructions are given by the Hoechst Colour Works for the application of their chromium mordants, *G.A. I.* and *G.A. II.*, to cotton. Chromic acid seems to act simply as an acid like other acids in these preparations, and to exert no mordanting or oxidising effect. It should be remembered that these mordants are sensitive to light. The solutions of commercial strength do not dissociate.

Chromium Mordant, G.A. I. (M.L.B.), is recommended by the manufacturers for mordanting loose cotton, cotton yarn, and piece goods. It is a basic salt, containing chromium hydroxide, chromic acid, and hydrochloric acid.

The well-wetted material is steeped in the mordant, which has been diluted with water (1 to 4) for 12 to 24 hours, wrung out, and carefully rinsed in water; or it is worked before rinsing for 20 to 30 minutes in a weak soda-bath at 60° (1 part of soda ash in 200 of water). Alizarin red and Alizarin brown require a stronger mordant (1 part of mordant to 2 parts of water). Piece goods are padded in a solution of 1 part of mordant and 2 to 4 parts of water, rolled up moist, left well covered up, and finally passed through a weak soda solution as before.

Chromium Mordant, G.A. II. (M.L.B.).—This mordant (which is also a basic salt containing chromium hydroxide, chromic acid, and acetic acid) is, according to the makers, specially adapted for the drying and steaming process, since after drying it is easily and completely fixed by a slight steaming. Instead of steaming, the material can be aged for 24 hours; on account of the sensitiveness of these mordants to light, the ageing must take place in a dark room.

For steaming, 1 litre (1 gall.) of mordant *G.A. II.* is diluted with 4 litres (4 galls.) of water, and 80 to 100 c.c. (1 pint) of glycerin is added. The pieces are padded with this solution, dried and steamed for 10 to 20 minutes without pressure,and fixed as stated before.

Mordant *G.A. II.* can also be applied by printing.

A mixture of chromium chromate and chromium lactate has been recommended by C. H. Boehringer Sohn for cotton and silk. The mordant is prepared by mixing 10 parts chromium chromate, 64° Tw., and 40 parts chromium lactate, 12° Tw., and the cotton or silk is steeped in this solution, wrung, and carefully dried at 30° C., or steamed for one hour without pressure.

A mixed mordant of chromium hydroxide and zinc hydroxide has been recommended for Gallocyanin, and may be suitable for other mordant colours. The cotton is steeped for some hours in basic chromium chloride, 32° Tw., wrung out, and passed through a cold solution of sodium zincate, 3° Tw., wrung again, rinsed, and exposed to the air. A double mordant of zinc and chrome is thus produced. Sodium zincate is produced by dissolving zinc or zinc oxide in caustic soda lye (free of carbonate of soda), or by adding so much caustic lye to the solution of a zinc salt that the precipitate formed at first redissolves (see under *Zinc*). The mordanting baths may be used continuously.

(3) *Bichromates as Chromium Mordants.*—Bichromate has been employed for mordanting cotton by being incorporated with the fibre, and subsequently reduced with some oxidisable salt by steaming. For yarns the processes are

not practicable. H. Koechlin * has proposed the following method, which was for a long while unrivalled:—

800 grms. (8 lbs.) potassium bichromate, and
600 c.c. (5 pints) ammonia are dissolved in
2 litres (2 galls.) water;
800 grms. (8 lbs.) thiosulphate of soda,
½ litre (½ gall.) magnesium acetate (52° Tw.), and
4 litres (4 galls.) tragacanth thickening (60 to 1,000)

are added. The pieces are padded with the resulting mixture, dried, and steamed for one and a half to two hours, thus fixing chromic oxide and magnesia on the goods in the form of a very active and fast mordant, yielding a double lake. Thiosulphate is replaced with advantage by sodium or ammonium sulphocyanide, since this salt prevents a tendering of the fibre. The various salts have no action on each other at the ordinary temperature if the light is excluded; but the bichromate is reduced under the influence of steaming in the presence of magnesium acetate by the thiosulphate or sulphocyanide, and chromic oxide is deposited in the fibre. This process requires a long continued and strong steaming, and, in consequence of the formation of oxycellulose, owing to the reduction of the chromic acid, often causes a tendering of the goods.

Another method, patented by E. Knecht, the principle of which was proposed by Prudhomme, is to reduce a chromate with a sulphite. H. Koechlin has indicated the following mode of procedure:—50 grms. (½ lb.) potassium bichromate, 100 grms. (1 lb.) bisulphite of soda (56° Tw.), and 100 grms. (1 lb.) ammonia are made up to 1 litre (1 gall.); better results are obtained, according to W. M. Gardner, by using more bisulphite, 260 grms. (2·6 lbs.). The ammonia and bisulphite are first mixed, and then added to the solution of the bichromate. The mixture, which contains a large excess of ammonia, does not deposit any sediment; but if the ammonia is driven off by boiling or is allowed to evaporate, the chromate is at once reduced and chromic hydrate formed. Cotton piece goods are impregnated with the solution, dried, and steamed; the process yields good results without any tendering of the fibre taking place.

Richard and Santarini† state that still better results are produced by twice padding the piece with 20 parts bichromate of soda, 20 parts water, 40 parts bisulphite 66° Tw., and 16 parts formaldehyde, followed by drying at full width through the hot flue, three to four minutes steaming, and treatment for at least twelve minutes in a bath of caustic soda 4½° Tw. at 80°, washing and soaping; bisulphite and formaldehyde should be mixed in advance, but not more than a quarter of an hour before use. Instead of 40 parts of bisulphite, 12½ parts Hydrosulphite NF or Hyraldite A with 25 parts formaldehyde may be used.

Max Becke‡ has published a very interesting method; the principle of the method is to reduce chromic acid in the presence of the fibre by means of aniline. A more or less dark shade of Aniline-grey is thus fixed along with a certain proportion of chromic oxide. The cotton prepared in this manner can subsequently be dyed with colouring matters which possess affinity for chromic oxide.

J. J. Hummel has suggested that the vegetable fibre should be mordanted with tannin, and subsequently treated with a boiling solution of bichromate. We find that up to 20 per cent. tannic acid, or a corresponding quantity of sumach, &c., is necessary for full shades; the bichrome bath is prepared with 1 part of sulphuric acid for 3 parts of bichromate. In a similar way, goods which have been dyed with cutch and developed in bichrome become

* *Journ. Soc. Dyers and Col.*, 1885, p. 25. † *Ibid.*, 1907, p. 124.
‡ *Ibid.* 1888, p. 24.

mordanted with chrome, and may subsequently be topped with mordant dyes, like logwood, fustic, Alizarin, &c.

Compounds of chromium find but little employment in *jute* dyeing, since this fibre is seldom dyed with mordant colours.

Application to Wool—(1) *Chromium Salts as Wool Mordants.*—Apart from chromium fluoride, chrome-alum is the only salt of chromic oxide that has been employed for wool-mordanting. The amount of chromium fixed from chrome-alum is about twice as great as that fixed by equivalent percentages of bichromate under the same conditions.* Probably a part of the chromium sulphate is simply absorbed by the wool fibre, and is not fixed in a permanent manner, since it yields in dyeing greatly inferior results to the bichromate. To obtain good and full shades with chrome-alum, it is found necessary to use for each equivalent of chrome-alum from 12 to 18 equivalents of tartar.†

The salts of chromium have not been so thoroughly investigated as those of aluminium in their behaviour towards wool; we have seen, however, that they are considerably less easily dissociated; if, then, the hypothesis be correct that the wool fibre dissociates aluminium salts, and combines with the alumina, we may suppose that the wool does not readily dissociate chromium sulphate, and that it appropriates only a small amount of this mordant when the amount of tartar present is not excessive; this would account for the unsatisfactory results with chrome-alum.

Chromium fluoride has frequently been recommended, and it has been asserted that it would take the place of potassium bichromate in wool dyeing. This, however, has not been realised, possibly because chromium fluoride is not well applicable in the presence of copper, and the wool receives a harsh feel. The price of chromium fluoride is also considerably higher than that of the bichromates. Chromium fluoride seems particularly useful where bichromate is injurious owing to its oxidising action. Comparative experiments‡ have shown that if a quantity of chromium fluoride, amounting to 1 per cent. of the weight of the wool, is used as a mordant, all the chromium is fixed on the fibre; while an equivalent quantity of potassium bichromate gives up only one-half of its available chromium. By employing as much of the chromium fluoride as amounts to 2 per cent. of the weight of the wool, 78 per cent. of the chromium is fixed, and in using 4 per cent. chromium fluoride nearly 70 per cent. is taken up by the fibre, whereas about 60 per cent. of the equivalent bichromate is left in the bath. The mordanting proceeds in a similar way as with bichromate; 4 per cent. chromium fluoride and 2 per cent. oxalic acid (of the weight of the wool) are used. The baths can be used continuously after being freshened up each time; care must be taken, however, that the amount of oxalic acid in the mordanting-bath does not become too large.

Wooden dye-vats with lead pipes for heating should be used for the application of the fluoride.

(2) *Chromic Acid as a Wool Mordant.*—Chromic acid in the form of bichromates of potassium and sodium is the most important and most generally used wool mordant; it offers the great advantages of being cheap and easily applied, as also of yielding full, brilliant, and fast colours. With a comparatively very small amount of the salt deep colours are obtained. The mordanting-bath is prepared with 2 to 4 per cent. potassium bichromate (of the weight of the wool) and the necessary quantity of water, amounting to from 50 to 100 times the weight of the wool. The wool is boiled for 1 to 1½ hours with this liquor, and, after being washed in water, is ready for dyeing. Sulphuric acid (1 to 3 per cent. of the weight of the wool) is sometimes added to the bath either for

* Kay and Bastow, *Journ. Soc. Dyers and Col.*, 1887, p. 118.
† W. M. Gardner, *Journ. Soc. Dyers and Col.*, 1890, p. 37.
‡ *Journ. Soc. Dyers and Col.*, 1891, p. 121.

the purpose of rendering the action of the mordant more energetic or of keeping the composition of the bath constant. The wool which has been mordanted in this way with or without acid assumes a yellow colour, and probably contains chromic acid. Under the influence of the active rays of light this colour is changed to green (see *Chromium Trioxide*), probably by reduction of the trioxide to chromic oxide. Goods which have been affected in this way are liable to dye unevenly and to have a speckled appearance. Passing through a bisulphite solution before dyeing may remedy this fault.

Hydrochloric and nitric acid, according to J. J. Hummel and W. M. Gardner,* differ materially in their action from sulphuric acid, effecting an almost complete exhaustion of the mordanting-bath.

More brilliant colours are obtained when organic acids or acid salts (for example, formic or oxalic acid or tartar) are used along with the bichromate. The latter is partly reduced, and chromic hydroxide formed on the fibre. In this case the wool has a greenish colour, like that of the chromium salts and chromic hydroxide. The quantity, however, of organic substances usually employed is not always sufficient to reduce the whole amount of bichromate that is extracted from the bath by the fibre. Up to a few years ago tartar was employed most generally as an assistant for mordanting with bichromates, 3 per cent. of bichrome and 2½ per cent. of tartar being the usual quantities, or, for very dark shades, 4 per cent. of bichrome and 3 per cent. of tartar. Sometimes oxalic acid was used on account of its lower price, although its action as regards even mordanting and good reduction of the bichromate is inferior; for 3 to 4 per cent. of bichrome about 1 to 2 per cent. of oxalic acid was employed. During the last few years lactic acid, lactoline, and lignorosine have come very generally into use; they exert a very good reducing effect, and the mordant is satisfactory and fairly evenly fixed. The proportions recommended are 2 to 3 per cent. of bichrome and 3 to 5 per cent. of lactic acid, with or without the gradual addition of 1 to 1½ per cent. of sulphuric acid; or 1½ per cent. of bichrome and 3 per cent. lactoline; or 2·7 per cent. bichrome, 4·5 per cent. lignorosine, and 1·8 per cent. of sulphuric acid for dark shades; and, for light ones, 1·3 per cent. of bichrome, 2·7 per cent. lignorosine, and 0·8 per cent. sulphuric acid. Recently formic acid has been introduced by S. Kappf † as a very effective assistant which exhausts the chrome bath entirely, and makes it possible to mordant even the deepest shades with only 1½ to 2 per cent. of bichrome and the same quantity of formic acid.

Another way of reducing the chromic acid is to pass the mordanted wool through a tepid solution of bisulphite of soda containing about 5 per cent. liquor (60° Tw.), calculated on the weight of the wool (E. Knecht).‡ Treated in this manner the chrome becomes more completely reduced than if tartar had been used; and the results obtained in dyeing are much better with a large number of adjective dyes, notably logwood, Alizarin-blue, Coeruleïn, and Galleïn.

O. T. Amend recommends free chromic acid for mordanting wool. The dry wool is entered in a bath which contains 6 per cent. acetic acid, and is heated to 75° to 80°; after one-half hour's working 1 per cent. chromic acid is added, and the working continued for thirty minutes more, when 6 per cent. sodium bisulphite is added, and the liquor is re-heated to 75° to 80°, whilst the wool is turned one-half hour more; after this the wool is rinsed, or simply allowed to drain, and then dyed with the addition of 1 per cent. ammonia without acid. Chromic acid may be replaced by a mixture of bichromate and sulphuric acid.§

If a large excess of bichromate, especially in conjunction with sulphuric acid, is used, it exerts an injurious effect on some colouring matters by oxidis-

* *Journ. Soc. Chem. Ind.*, 1895, p. 452.

† *Journ. Soc. Dyers and Col.*, 1905, p. 75. ‡ *Ibid.*, 1889, p. 186.

§ R. Loewenthal, *Lehne's Färberzeitung*, 1899, p. 303.

ing them and destroying their colouring principle, while at the same time the fibre is injured. Wool so treated is said to be "*overchromed.*" Small amounts of bichromate do not exert this influence to so large an extent, but the products of oxidation diminish the brilliancy of the ultimate colour more or less, and the excess of mordant bleeds out and precipitates the colouring matter in the dye-bath, and this being more or less taken up mechanically by the wool gives rise to colours which rub-off. The reduction of the bichromate previous to dyeing not only prevents this loss from overchroming, but also, by checking the decomposition of the colouring matter, allows of more brilliant shades being obtained.

R. L. Whiteley * boiled wool in a solution of potassium bichromate and then removed as much of the salt as could be extracted by repeated treatments with cold water for several weeks. The wool still contained a considerable quantity of chromic acid in some form, as was shown by the formation of Chrome-yellow on the fibre when it was passed through the solution of a lead salt. Kay and Bastow (*l.c.*) found that in boiling wool with potassium bichromate the bichromate is decomposed and a certain amount of potassium chromate is found in the mordanting liquor. These facts indicate that the potassium bichromate is partly absorbed by the wool fibre and partly decomposed, its acid constituent being partly extracted and retained by the fibre as chromic acid, expressed by the equation—$K_2Cr_2O_7 = K_2CrO_4 + CrO_3$.

Nietzki † has explained this fact by assuming that the chromic acid is partially reduced by the wool fibre to chromium chromate. Chromium chromate is but little known, and it is improbable that under the conditions prevalent in the mordanting-bath—boiling temperature and great dilution—chromium chromate would be formed from chromium oxide and chromic acid, or that it could exist without dissociating.

J. J. Hummel ‡ contends that, if oxidation of the wool does take place, it is very slight, and, certainly, only a secondary accompaniment, not, by any means, the essential action, which accounts for the striking character of the mordanting powers of potassium bichromate.

Knecht, § in view of the great affinity of wool for acids, argues that the mordanting of wool with bichromate is simply due to a dissociation of the salt into chromic acid (which combines with the substance, or a constituent of the substance, of the wool fibre) and the normal potassium chromate ‖ (which remains in the bath). During the dyeing, chromic acid is reduced partly by the dyestuff, partly by other substances present, and partly by the wool fibre, whereby it is converted into the mordant proper—chromium hydroxide.

Knecht (*l.c.*, 1889, p. 184) has compared the quantities of chromic acid which wool takes up under equal conditions from (1) neutral potassium chromate, (2) potassium bichromate, and (3) chromic acid (potassium bichromate mixed with one equivalent of sulphuric acid). He found that most was fixed from chromic acid and least from neutral chromate.

In mordanting with 3 per cent. bichromate (the amount usually employed on the large scale) only about 1 per cent. is fixed by the wool, as shown by experiments in the laboratory, and by analysing a series of mordant-liquors used in a dye-works. Usually dyers work their bichromate bath continuously, freshening up the same after each operation with a *greater* amount of bichromate than has been consumed. Analyses showed (*l.c.*) that the amount of

* *Journ. Soc. Chem. Ind.*, 1887, p. 131.

† *Journ. Soc. Dyers and Col.*, 1889, p. 161. ‡ *Dyeing of Textile Fabrics*, p. 209.

§ *Journ. Soc. Dyers and Col.*, 1889, p. 186; *ib.*, 1888, p. 104.

‖ This has been definitely proved by the more recent researches of Abegg and Cox (*Journ. Soc. Dyers and Col.*, 1905, p. 114), who show that in very dilute solutions the dissociation is complete. At a concentration of 1 grm. per litre it amounts to 62 per cent. and at one of 0·1 grm. per litre to 91 per cent.

bichromate remained almost constant at 0·5 grm. per litre when 3 per cent. bichromate was used the first time, and as much added after each operation; but the neutral chromate steadily increased up to an amount equivalent to at least 3·24 grms. of the bichromate per litre, when the bath had to be let off. A great quantity of chromium is thus lost every day, since the baths become overcharged with the salts, and have to be thrown away. Knecht therefore recommends that no more bichromate be added to the bath than is necessary to replace the amount extracted by the wool, as also that as much sulphuric acid be supplied as will reconvert most of the chromate into bichromate.

It would well repay the dyer to make rough tests of his "chrome" baths from time to time both as regards *condition* (acidity or alkalinity as the case may be) and as regards the amount of chromate present. In order to test the condition of the bath, the best *indicator* is *lackmoid paper* (see *Analysis*, Part XI.). If the whole of the chromium is present in the form of *bi*chromate, the paper shows a neutral reaction; if normal chromate be present red paper is turned blue, whereas an excess of acid turns blue lackmoid paper red.

To find the amount of acid to be added, the following simple method is recommended:—Take 1 litre of the chrome liquor and pour it into a white porcelain basin. Gradually add from a burette, with constant stirring, a solution of sulphuric acid containing 6 grms. per litre until a piece of blue lackmoid paper shows a neutral reaction. The number of cubic centimetres required to produce this effect corresponds to the number of ounces of sulphuric acid (D.O.V.), to be added to 1,000 gallons of "chrome liquor."

In order to find the amount of chromate and bichromate present in a vat, the following mode of procedure is, perhaps, the simplest:—Weigh 1 grm. of granulated ferrous ammonium sulphate into a porcelain basin, add 100 cubic centimetres of a 2 per cent. solution of sulphuric acid, and run in from a burette the chrome liquor until a drop of the solution ceases to produce a blue colour when brought in contact with a drop of potassium ferricyanide. The number obtained by dividing the figure 126 by the number of cubic centimetres of "chrome" liquor required, equals the number of pounds of potassium bichromate in 100 gallons.

Practical experience has shown that a chrome bath works better after it has been used two or three times than when fresh. This would indicate that it is best to have a mixture of normal chromate and bichromate in the bath, and that only so much acid should be added as will keep the liquor in this state. W. M. Gardner and T. Carter * attribute the condition to a certain extent to the presence in the bath of "wool-gelatine."

The oxidising action of bichromate and chromic acid is especially detrimental in the case of mordanting vat-dyed wool, since a part of the indigo is destroyed. In order to preserve the indigo the wool is mordanted either with bichromate without any assistants or with the addition of small quantities of tartar or lactic acid or lignorosine, whilst sulphuric or oxalic acids must be absolutely avoided, and also the addition of blue vitriol, a very great proportion of the indigo being destroyed by their action. A mixture of bichromate, blue vitriol, and sulphuric acid is even very well adapted for destroying colours on shoddy material and mordanting the fibre simultaneously for re-dyeing

Application to Silk.†—For the mordanting of silk with chromium compounds normal or basic chromium salts are used. Bichromate does not serve as a mordant proper, although it is used as an oxidising agent in the developing of Cutch browns.

Ungummed silk is steeped for six hours in a strong solution of a chromium salt (*e.g.*, basic chromium chloride, 32 Tw.), well wrung, washed, worked in

* *Journ. Soc. Dyers and Col.*, 1898, p. 167. † See also P. Heermann, *l.c.*, p. 238.

silicate of soda ($\frac{1}{2}$° Tw.) for fifteen minutes, and again washed; it is then ready for dyeing.

Chromium Mordant, G.A. III. (M. L. B.), is recommended by the makers for wool-printing, and especially for dyeing the Alizarin colours on silk. It consists of chromium chromate, $Cr_2(CrO_4)_3$.

Discharged silk is steeped for twelve to twenty-four hours in the mordant (1 part diluted with 4 parts water), and is ready for dyeing after simply washing with water.

IRON (*Ferrum*), Fe = 55·9.

Iron is divalent in some compounds and tetravalent in others, or trivalent according to recent opinions. Its specific gravity is 7·84. In pure air and in oxygen it does not tarnish. Pure water does not act on iron below red heat, but water containing carbonic acid and air oxidises it, forming rust or ferric hydroxide. Steam is decomposed by iron at red heat, magnetic oxide of iron being formed and hydrogen liberated. Iron is dissolved by most acids with evolution of hydrogen, but cold diluted nitric acid dissolves it without evolving gases, and forms ferrous nitrate and ammonium nitrate. If iron is treated for a short while with cold strong nitric acid and then washed with water, it becomes passive, and is but slowly acted upon by chemical agents.

Iron forms four different compounds with oxygen:—

1. Ferrous Oxide, FeO.
2. Magnetic or Black Oxide of Iron, Fe_3O_4.
3. Ferric Oxide or Sesquioxide of Iron, Fe_2O_3.
4. Ferric Acid (Anhydride), FeO_3.

Of these the last named is known only in the form of some very unstable salts—*e.g.*, potassium ferrate, K_2FeO_4. This compound and the magnetic oxide are of no practical interest to dyers.

Ferrous Oxide, FeO, is a black powder which readily absorbs oxygen, passing into the higher oxides.

Ferrous Hydroxide or Hydrate, $Fe(OH)_2$, is a white mass in the pure state; but greenish when slightly oxidised. The moist hydroxide absorbs oxygen with avidity, changing first to green and then to brown. It is a weak diacid base, and is dissolved by acids with evolution of heat forming *ferrous salts.* Ferrous hydroxide is generated by the action of water containing air on iron. It dissolves in 150,000 parts of water, imparting to the latter an alkaline reaction and the peculiar taste of ferrous salts. Ferrous hydroxide is precipitated from solutions of ferrous salts by caustic alkalies, but is not redissolved by an excess of the precipitant. It is a fairly strong reducing agent which is made use of in the copperas vat.

Ferric Oxide, Fe_2O_3—*Sesquioxide of Iron.*—Iron sesquioxide occurs native in several minerals, and forms the red pigment *colcothar* or *caput mortuum.* It is obtained as a brownish-red powder by heating ferric hydroxide or a ferric salt of a volatile acid—*e.g.*, ferric sulphate. It dissolves slowly in acids. In ferric oxide, ferric hydroxide, and the ferric salts it was formerly supposed that two tetravalent iron atoms were combined and acted as a hexavalent group $\equiv$ Fe—Fe $\equiv$.

Ferric Hydroxide or Hydrate, $Fe(OH)_3$ or $Fe_2(OH)_6$, is precipitated as a brown voluminous mass from the solutions of ferric salts by caustic alkalies. The precipitate becomes denser in boiling water, being transformed into the *hydroxides*, $Fe_2O(OH)_4$ and $Fe_2O_2(OH)_2$. The precipitate is not redissolved by alkalies, but its formation may be prevented by organic substances such as glycerin. An alkaline solution of ferric hydroxide to which glycerin has been added has been proposed by H. Koechlin for the mordanting of cotton. The

ordinary ferric hydroxide is not soluble in water, but, under certain conditions, it can be brought into solution by dialysis; it possesses no affinity to the textile fibres. Such dialysed iron is used in medicine, and may be employed as an antidote for arsenic poisoning internally and externally.

Ferric Hydroxide is a weak tri-acid base. It does not form well defined salts with weak acids, but is readily soluble in most acids, forming with them *ferric salts*. Ferric hydroxide is soluble in neutral ferric salts, forming basic salts, and hence behaves like the aluminium and chromium hydroxides. These solutions, when greatly diluted and heated, are dissociated. Ferric hydroxide is slightly soluble in many organic substances, and imparts to them a yellowish to brown colour.

Ferrous Salts are white in the anhydrous state, but when they contain water they are greenish. They possess a sweet metallic taste, with an inky after-taste. Their aqueous solutions dissolve nitric oxide with a black colour. The soluble ferrous salts have an acid reaction. They are decomposed by strong heat. The caustic alkalies and lime precipitate ferrous hydroxide from the solutions.

Salts of ammonia prevent the precipitation by caustic ammonia completely, by other agents partially. The alkaline solution separates the ferric hydroxides in an insoluble state under the oxidising influence of the air. Organic substances, especially non-volatile acids and sugar, also impede the precipitation. Ammonium sulphide precipitates ferrous sulphide from neutral solutions of ferrous salts, and so does sulphuretted hydrogen from alkaline solutions.

The solutions of ferrous salts become turbid by absorbing oxygen from the atmosphere, forming basic ferric salts in the form of brownish flocculent precipitates. By other oxidising agents they are also readily oxidised. With potassium ferrocyanide they give a white precipitate, which rapidly becomes blue on exposure to the air; but with potassium ferricyanide a blue precipitate (Turnbull's blue) is immediately formed.

Ferric Salts.—Neutral ferric salts in the anhydrous state are nearly white; the hydrated neutral and the basic salts are yellow or reddish-brown. The aqueous solutions have a brownish-yellow colour, which turns reddish-yellow on heating. The soluble salts have an acid reaction, an astringent taste with an inky after-taste, and are decomposed on heating. Their solutions do not dissolve nitric oxide.

Ferric salts are obtained by the oxidation of ferrous salts with chlorine or nitric acid, and are easily reduced again—*e.g.*, by sulphuretted hydrogen, iron, stannous chloride, &c.

Caustic alkalies and their carbonates, lime, &c., precipitate from the solutions of ferric salts ferric hydroxide, which is not soluble in an excess of the precipitant, nor is it affected by the presence of ammonium salts. Organic substances impede the precipitation. Ammonium sulphide precipitates from the neutral, and sulphuretted hydrogen from the alkaline solutions of ferric salts black ferrous sulphide.

Potassium ferrocyanide produces in solutions of ferric salts a beautiful blue precipitate, which is insoluble in hydrochloric acid, but is destroyed by caustic alkalies. Potassium ferricyanide colours the solutions of ferric salts a fuller red-brown *without producing a precipitate;* the formation of a blue precipitate in such solutions indicates the presence of ferrous salts. Potassium sulphocyanide produces in acid solutions of ferric salts a very intense blood-red colouration which does not disappear on heating with a little alcohol (test for presence of ferric salts in ferrous salts). In the presence of acetates, oxalates, or fluorides, much hydrochloric acid should be added to be sure of the test. The soluble ferric sulphocyanide can be extracted with ether, and this extract will show the colour still better. The test is an exceedingly delicate one with a freshly-prepared solution of potassium sulphocyanide.

Ferrous Sulphate, $FeSO_4 + 7H_2O$—*Copperas; Green Vitriol.*—Ferrous sulphate is formed by dissolving iron in diluted sulphuric acid; it is prepared on the large scale from the iron pyrites or "dross" found in coal. The dross is exposed to the open air in clay-lined pits, and the liquors which collect are boiled with scrap-iron in order to reduce the ferric sulphate to ferrous sulphate; they are then evaporated down in leaden pans and allowed to crystallise. It is also obtained as a bye-product in various manufactures. The commercial product forms bluish-green monoclinic crystals, which effloresce in the air and become yellowish by oxidation, though when pure they are perfectly stable. Ferrous sulphate is readily soluble in water, sparingly in dilute alcohol, but is insoluble in absolute alcohol and in concentrated sulphuric acid. 100 parts of water dissolve of the crystallised salt, $FeSO_4 + 7H_2O$, at—

10° C.	15° C.	25° C.	60° C.	90° C.	100° C.
Parts. 61	Parts. 70	Parts. 115	Parts. 263	Parts. 370	Parts. 333

Solutions of ferrous sulphate do not dissociate either on heating, or on diluting; when oxidised by the air, however, insoluble basic ferric sulphates are precipitated, as exemplified in the equation—$10FeSO_4 + 5O = Fe_4SO_9 + 3Fe_2(SO_4)_3$.

Basic ferrous sulphates cannot be prepared.

Ferrous sulphate should not contain any copper, alumina, or zinc. Large crystals often contain free acid by enclosing some acid mother liquor. Ferrous sulphate is very extensively used in various industries. It is one of the most important and one of the oldest mordants known, and is still extensively employed, although it has been largely replaced in wool dyeing by chrome mordants. It is also used as a reducing agent in the so-called copperas vat.

Ferrous Chloride, $FeCl_2$, or *Muriate of Iron*, is obtained by dissolving iron in hydrochloric acid, and as a bye-product in the extraction of copper from spent oxide in the wet way. It forms deliquescent green crystals, having the composition $FeCl_2 + 4H_2O$.

Ferrous chloride is used for the production of logwood black in wool-printing and has also been met with as an adulterant in black liquor.

Ferrous Nitrate, $Fe(NO_3)_2$, is obtained by dissolving iron in cold diluted nitric acid (1·11 sp. gr.) according to the equation—$8Fe + 20HNO_3 = 8Fe(NO_3)_2 + 2NH_4NO_3 + 6H_2O$. It is known in solution only, and is decomposed by gentle heat, generating nitric oxide and basic ferric salt. It can also be obtained by the double decomposition of ferrous sulphate and barium nitrate.

Ferrous Carbonate, $FeCO_3$, is formed on addition of sodium carbonate to the aqueous solution of ferrous salts. It dissolves in water containing carbonic acid, forming an acid salt, the constituent of many ferruginous mineral waters.

Ferrous Acetate, $Fe(C_2H_3O_2)_2 + 4H_2O$.—This salt is obtained by dissolving iron in acetic acid, or by the double decomposition of ferrous sulphate and lead or calcium acetate. It forms green monoclinic prisms containing 4 molecules of water of crystallisation, and oxidises rapidly in the air, forming basic ferric acetate. As the iron must be brought to the fibre in the ferrous state, and be fixed by oxidation, the ferrous acetate is too unstable to be used as a mordant. It is sometimes employed to produce iron buff on cotton. Impure solutions of ferrous acetates form the very important mordant next mentioned.

Pyrolignite of Iron—*Iron Liquor, Black Liquor.*—This product is obtained by dissolving scrap-iron in the so-called pyroligneous or crude acetic acid. It

forms a dark olive-brown liquid of metallic taste and peculiar smell, and is made to stand at 20° to 30° Tw. The liquor can also be prepared by the double decomposition of ferrous sulphate and crude calcium acetate. Pyrolignite of iron consists principally of ferrous acetate, and contains a small amount of ferric acetate. It is generally supposed that the tarry matter from the crude acid prevents the oxidation of the ferrous salt. Moyret * has, however, shown that the presence of pyrocatechin alone is sufficient to impart all the characteristic properties—colour and stability—to ferrous acetate. Pyrocatechin and its methyl ether, guiajacol, are always present in pyroligneous acid, being products of the destructive distillation of wood.

Pyrolignite of iron is used in cotton dyeing, in greater quantities in calico-printing, and in black silk dyeing.

It may contain as impurities an excess of acetic acid, ferrous chloride, ferrous and ferric sulphate, calcium and lead acetate. The value of the mordant may be determined by a comparative dye trial.

Ferrous Oxalate, $FeC_2O_4 + 2H_2O$, is a crystalline lemon-yellow powder, almost insoluble in water. It is formed on mixing concentrated solutions of oxalic acid and of ferrous sulphate.

Ferrous Tartrate, $FeC_4H_4O_4$, is little known. It is only slightly soluble in water. By the action of tartar on iron filings ferrous potassium tartrate is obtained.

Ferric Sulphate, $Fe_2(SO_4)_3$, is obtained by adding nitric acid to a hot solution of ferrous sulphate, which contains the requisite amount of sulphuric acid—$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$. It can also be obtained by the prolonged action of concentrated sulphuric acid on ferric oxide.

The yellowish-brown solution yields on evaporation a syrupy liquid which deposits on standing small crystals containing water of crystallisation. Sulphuric acid precipitates from the concentrated solution anhydrous salt. The anhydrous salt dissolves but slowly in water; at high temperatures it is split up into ferric oxide and sulphuric anhydride.

By boiling the diluted solution, or by incomplete precipitation with alkalies, basic ferric sulphates are thrown down; the same products are formed by oxidation when ferrous sulphate is exposed to the air. A solution of ferrous sulphate yields on oxidation with nitric acid red crystals of the composition $Fe_2(SO_4)_2(OH)_2 + 14H_2O$. On dissolving in water they dissociate, forming an insoluble precipitate, $Fe_2(SO_4)(OH)_4 + 5H_2O$. Soluble basic ferric sulphates are obtained by addition of sodium carbonate to a solution of the normal sulphate—*e.g.*, the salts $Fe_2(SO_4)_2(OH)_2$ and $Fe_4(SO_4)_3(OH)_6$; they dissociate after some hours standing. Basic salts which are prepared by dissolving ferric hydroxide in solutions of the normal salt are more stable, but at the same time more expensive. The best way to prepare the basic ferric sulphates is to oxidise ferrous sulphate with nitric acid in presence of an amount of sulphuric acid insufficient to form the normal salt (see below).

Ferric sulphate is the chief constituent of commercial "nitrate of iron."

"Nitrate of Iron" (*Rouille;* Germ., *Salpetersaures Eisen*).—In cotton and silk dyeing a liquor which is called *nitrate of iron* is very extensively used. It is prepared by heating a solution of ferrous sulphate with nitric acid and sulphuric acid, and consists of ferric sulphate, basic ferric sulphates, and ferric sulphate-nitrates. It does not contain, however, ferric nitrate or ferrous nitrate; hence the name "nitrate of iron" is a misnomer.

Normal ferric sulphate is obtained by the action of nitric and sulphuric acid on ferrous sulphate according to the equation which has been stated

* *Teinture des soies*, Lyons, 1878, p. 197.

above. If a smaller quantity of sulphuric acid or none at all is added, basic ferric sulphates are obtained, for example—

$$6FeSO_4 + 2HNO_3 + 2H_2O = 3Fe_2(SO_4)_2(OH)_2 + 2NO.$$

Normal and basic ferric sulphate-nitrates are produced when the quantity of nitric acid is increased, as shown by the equations—

$$1.\ 6FeSO_4 + 8HNO_3 = 3Fe_2(SO_4)_2(NO_3)_2 + 2NO + 4H_2O.$$
$$2.\ 6FeSO_4 + 5HNO_3 = 3Fe_2(SO_4)_2(NO_3)(OH) + 2NO + H_2O.$$

Basic salts can also be prepared by adding caustic soda to the solutions of normal "nitrate of iron"; they dissociate, however, after a few hours; hence the product should be prepared from the beginning as basic as required by using the corresponding quantities of acids. Basic salts which have been prepared by dissolving ferric hydroxide in nitrate of iron are more stable than those obtained with caustic soda; but they are too expensive.

Liechti and Suida * have examined a number of commercial brands of nitrate of iron, and prepared the following compounds:—

1. $Fe_4(SO_4)_5(OH)_2$.
2. $Fe_2(SO_4)_2(OH)_2$.
3. $Fe_2(SO_4)_2(NO_3)(OH)$.

Most of the commercial products were found to correspond to the first formula, which was also found to be the best for silk dyeing by Moyret,† $Fe_2(SO_4)_{2\cdot7}$. One mordant which gives excellent results and is largely used in Crefeld is intermediate between the normal salt $Fe_2(SO_4)_3$ and that represented by formula No. 1. It nearly corresponds to the composition $Fe_2(SO_4)_{2\cdot7}$, and contains 11·5 per cent. total iron (0·5 per cent. iron in the ferrous state) and 27·2 per cent. "SO_4."

The first compound can be produced according to the equation—

$$12FeSO_4 + 3H_2SO_4 + 4HNO_3 = 3Fe_4(SO_4)_5(OH)_2 + 4NO + 2H_2O.$$

This equation demands for 72 parts of ferrous sulphate 6·3 parts of sulphuric acid and 12·6 parts of nitric acid (67° Tw.). Moyret † gives in his book the following prescription which corresponds fairly well to this equation:—

A large closed vessel (constructed of stone, cast iron, or even wood) is provided with a wide tube for the escape of the nitrous gases and with openings for the introduction of the materials and for a mixer. For 100 parts of nitrate of iron (90° Tw.) 72 parts of ferrous sulphate are necessary, or somewhat more, if the crystals contain much mother liquor. The requisite amount of ferrous sulphate is brought into the vessel, and after this has been closed a mixture of 6 to 7 parts of sulphuric acid (168° Tw.) and 10 to 15 parts of nitric acid (67° Tw.) diluted with a little water are poured gradually on to the crystals and the mixture is stirred. A reaction sets in and nitrous gases are given off which can be condensed in *bombonnes*. The reaction is first allowed to proceed at the ordinary temperature, and after it has subsided it is completed by blowing steam in. When no more gases are given off the reaction is complete and the liquid is transferred to reservoirs to cool and to settle. The reaction must be well regulated in order that it may not become too violent, otherwise insoluble basic ferric sulphates are formed whereby loss is caused and the remaining solution will not become basic enough.

The product has a deep red colour, and should contain about 17 per cent. of ferric oxide and but very little ferrous salt or hydrochloric acid; it should not give a precipitate with silver nitrate, and, when diluted with much water,

* *Journ. Soc. Dyers and Col.*, 1885, p. 60. † *Teinture des soies*, Lyons, 1878, pp. 203 and 205.

should give only a blue colouration but no precipitate with red prussiate of potash. Ferric chloride dissociates very incompletely, and ferrous sulphate impedes the dissociation; the same is the case with sodium sulphate, hence the presence of these salts is objectionable. The commercial products contain, as a rule, some nitric acid which has escaped decomposition. Products of the same composition vary often in their tinctorial properties, especially for silk dyeing; and their value is best estimated by comparative dye-trials.

Ferric sulphate-nitrates are also sold under the name of nitrate of iron. The way to prepare them has been indicated above. In oxidising ferrous sulphate the sulphuric acid is partly or entirely replaced by nitric acid. The products are deep brownish-red solutions of varying composition, and frequently contain ferrous salt. In cotton dyeing an admixture of the latter salt is sometimes advantageous. The value is also determined by the results they give in experimental dyeing. The ferric sulphate-nitrates are used almost exclusively in cotton dyeing. On the whole, "nitrate of iron" brands which are used for cotton are slightly less basic than those made for silk dyeing.

Iron Alum or Potassium Ferric Sulphate, $Fe_2K_2(SO_4)_4 + 24H_2O$, forms light-violet octahedra, and is soluble in about 5 parts of cold water. It is analogous to ordinary alum and the other alums. Iron alum is not used to any great extent in dyeing.

Ferric Chloride, $FeCl_3$ or Fe_2Cl_6.—A solution of ferric chloride is obtained by dissolving ferric hydroxide in hydrochloric acid, or by oxidising a solution of ferrous chloride with nitric acid, with the addition of the required amount of hydrochloric acid. The concentrated solution is dark brown and viscid. The aqueous solution dissociates on heating, and the dissociation point is lower the greater the dilution. If the solution is not too much diluted the normal chloride is regenerated on cooling. Basic chlorides are obtained by several methods, and some are soluble while others are insoluble in water.

The ferric chlorides, both the normal and the basic, dissociate too slowly to be applicable in dyeing.

Ferric Nitrate, $Fe(NO_3)_3$ or $Fe_2(NO_3)_6$—*Nitrate of Iron.*—This salt is prepared by slowly dissolving iron in nitric acid. When a precipitate of insoluble basic ferric nitrate begins to form the reaction is complete, and no more iron is added. A brown-red liquor is obtained, the composition of which varies. Moyret gives the formula $Fe_2(NO_3)_5OH$. Ferric nitrate is sometimes employed in silk dyeing; it finds a limited application in black dyeing and in producing iron-buffs and Prussian blues on cotton.

Ferric Sulphocyanide or Thiocyanate, $Fe_2(CNS)_6$, is obtained as a blood-red solution by dissolving ferric hydroxide in sulphocyanic acid, or by the double decomposition of ferric salts and sulphocyanides.

Ferric Phosphates.—On addition of phosphate of soda to ferric salts, a yellowish-white precipitate of ferric phosphate, $FePO_4$ or $Fe_2(PO_4)_2$, is obtained, which is soluble in diluted mineral acids, but insoluble in acetic acid. (The precipitation becomes complete on addition of sodium acetate.) On this reaction is based the fixation of iron mordants with phosphate of soda.

A solution of ferric pyrophosphate, $Fe_4(P_2O_7)_3$, in ammonia has been recommended by Persoz as a cotton mordant.

Ferric Arsenate.—Sodium arsenate produces in solutions of ferric salts a white precipitate of ferric arsenate, $FeAsO_4$ or $Fe_2(AsO_4)_2$, which is insoluble in acetic acid, but soluble in ammonia with a brown-red colour. Arsenate of soda is used to fix iron mordants on cotton in Alizarin dyeing.

Ferric Acetate, $Fe(C_2H_3O_2)_3$ or $Fe_2(C_2H_3O_2)_6$, is obtained by the double decomposition of ferric sulphate and lead acetate, and forms dark red tablets containing two molecules of water of crystallisation. Basic salts can be prepared by addition of caustic soda to the solution of the normal salt. According

to Liechti and Suida, the normal salt does not dissociate either on heating or diluting with water. The basic salts are dissociated by heat, and all the iron is thrown down on boiling. Increase in basicity, as a rule, lowers the dissociation point; in diluted solutions, however, the dissociation point of the salt $Fe_2(C_2H_3O_2)_5OH$ is raised, that of $Fe_2(C_2H_3O_2)_4(OH)_2$ remains unchanged, whereas that of the more basic salts is lowered. The basic acetates are not dissociated by mere dilution with water.

Ferric acetates were extensively used in former years for black-dyeing the best qualities of silk, but they seem to have been replaced completely by nitrate of iron.

Ferric Nitrate-Acetate is prepared in the following way, according to Moyret:—Iron turnings are dissolved in nitric acid until the whole becomes a pasty mass of insoluble basic ferric nitrate, and this mass is subsequently dissolved in hot acetic acid, leaving a slight excess of the basic nitrate undissolved. A deep red solution is obtained, which is employed for the black-dyeing of silk intended for plush, because the colour it yields is not affected by hot-pressing.

Ferric Oxalate, $Fe_2(C_2O_4)_3$, is soluble in water, with a green colour. The solution is partly reduced to ferrous oxalate with evolution of carbon dioxide, both by boiling and by the action of light.

Ferric Tartrate, $Fe_2(C_4H_4O_6)_3$, is very little known.

Alkaline Iron Mordants (*Ferrites*).—Ferric hydroxide does not dissolve in caustic alkalies; the presence, however, of certain organic substances, notably glycerin or glucose, in solutions of ferric salts prevents the precipitation of the ferric hydroxide by alkalies, and thus an alkaline solution of ferric hydroxide can be prepared, which readily dissociates. Koechlin * has recommended the following mixture for preparing cotton piece goods:—2 measures of nitrate of iron (76° Tw.), 2 measures of caustic soda (66° Tw.), and 1 measure of glycerin (48° Tw.). Burgemeister proposed a ferrous hydroxide solution to be prepared by mixing 1 kg. (1 lb.) of ferrous sulphate, 60 litres (6 galls.) of caustic soda (70°), and 2 litres (1½ pints) of glycerin. These alkaline mordants have hardly found practical application, since they are expensive, and their strong alkalinity is objectionable. An alkaline mixture has been used for a long time, according to S. Balanche, in an Alsatian print works, to produce buff-yellow shades on cloth for linings. 20 parts of nitrate of iron (80° Tw.), 60 parts of glycerin, and 20 parts of ammonia are mixed and suitably diluted. The goods are impregnated with the mixture, and exposed to the air, when the ammonia is volatilised, and insoluble ferric hydroxide remains in the fibre.

Prussian Blue.—By the reaction of ferrous and ferric salts with yellow and red prussiate of potash, several compounds are produced.

Yellow prussiate and ferrous salts produce together a white compound, which oxidises rapidly in the air to form Prussian blue. The white compound probably has the composition $K_2Fe(CN)_6Fe$. Ferric salts produce in a solution of yellow prussiate which contains an excess of prussiate a blue precipitate of *ferric potassium ferrocyanide*, $K_2Fe_2(CN_{12})Fe_2$. This substance, usually called *Soluble Prussian blue*, dissolves, when pure, in water with a blue colour, and is precipitated from the solution by salts.

Turnbull's blue or *ferrous ferricyanide*, $Fe_5(CN)_{12}$, or $(Fe_2)_2(Fe_2)_3(CN)_{24}$, is formed by precipitating ferrous sulphate with red prussiate, and, finally, *Williamson's blue* or *Insoluble Prussian blue*, or *ferric ferrocyanide*, $Fe_7(CN)_{18}$ or $(Fe_2)_4(Fe_2)_3(CN)_{36}$, is obtained, together with the soluble form, when a solution of yellow prussiate is added to a solution of ferric chloride. The same compound is obtained by the action of chlorine or nitric acid on Turnbull's blue, or by precipitating the soluble Prussian blue with ferric chloride.

* *Journ. Soc. Dyers and Col.*, 1885, p. 18; *ib.*, 1885, p. 147.

The *pigment Prussian blue* is prepared by precipitating a solution of copperas with yellow prussiate of potash and oxidising the white product with nitric acid. It forms an intensely blue powder or lumps having a coppery lustre, and consists of mixtures of the various blues. It is quite insoluble in water, but dissolves in ammonium tartrate with a violet, and in oxalic acid with a blue, colour. It is insoluble in the mineral acids and is not affected by them, but it is decomposed by alkalies with formation of ferric hydroxide and ferrocyanide; for instance—

$$Fe_7(CN)_{18} + 12KOH = 3K_4Fe(CN)_6 + 4Fe(OH)_3.$$

Hydroferrocyanic acid, $H_4Fe(CN)_6$ (or an acidulated solution of yellow prussiate), is dissociated on boiling; hydrocyanic acid escapes, while a white precipitate of an acid ferrous ferrocyanide is formed—$2H_4Fe(CN)_6 = 6HCN + H_2Fe(CN)_6Fe$. The same reaction is used for the preparation of hydrocyanic acid.

If an oxidising agent is present—*e.g.*, red prussiate—the reaction is somewhat different, and Williamson's blue is formed together with hydrocyanic acid—$H_4Fe(CN)_6 + O_2 = Fe_7(CN)_{18} + 24HCN + 2H_2O$. Use is made of this reaction for the production of Prussian blue in wool dyeing and in calico-printing. In the latter case a mixture of yellow and red prussiate and tartaric acid, with or without the addition of stannous chloride, is printed on the material and then steamed.

APPLICATION OF THE IRON SALTS TO THE TEXTILE FIBRES.

Iron salts are very extensively applied in dyeing and printing. Ferrous sulphate serves as a reducing agent in the preparation of the indigo-vat (lime and copperas vat); hydrated ferric oxide is precipitated in the fibres to produce iron-buff shades and Prussian blue; and sometimes ferric salts serve as oxidising agents—*e.g.*, to prevent Aniline black from turning green. The applications of iron salts in dyeing for mordanting purposes and for weighting silk which is to be dyed black are of great importance. This last operation cannot be considered a mere mordanting, since much more of the mordanting body is deposited in the silk fibre than would be required to obtain the desired shade, the intention being to increase the weight and bulk of the silk.

Application to Cotton and Linen.—(1) *Ferrous Sulphate* or *Copperas* is used in cotton dyeing. Its use, however, has been greatly diminished of late by the introduction of the direct cotton colours and the sulphide colours. It is applied on tannin exactly like the ferric salt, and is also used similarly in the production of iron-buff shades. Sometimes it is used for darkening or "saddening" certain Aniline colours which have been previously fixed with a tannin-mordant. In many cases the material (pieces) is first impregnated with a boiling decoction of a natural dyestuff or mixture of dyestuffs, such as logwood, fustic, peachwood, cutch, &c., and subsequently passed through a cold solution of ferrous sulphate.

Probably the commonest way of applying copperas in cotton dyeing (especially for blacks) is to prepare with tannin, pass through clear lime water, and then through the copperas solution, or through the latter before the lime water. By the double decomposition of the calcium tannate and copperas, ferrous tannate is fixed on the fibre and calcium sulphate is formed, which is subsequently removed by washing. The ferrous tannate is rapidly oxidised in the air to ferric tannate.

Ferrous sulphate leaves only a very small quantity of iron on the fibre by

impregnating (padding) and ageing, hence it cannot be advantageously applied by this method.

(2) *Ferrous Acetate* or *Black Liquor* is not much employed in yarn dyeing, since for this material it offers no advantage over nitrate of iron, which is a cheaper article. It can be applied exactly like this product on goods previously mordanted with tannin. In the dyeing of cotton piece goods and in calico-printing it has been extensively used as a mordant in the production of blacks, purples, browns, &c. Ferrous acetate is applied exactly like aluminium acetate, by impregnating the fibre, drying, and ageing. But there is this difference, that the aluminium salt is merely fixed by the loss of acetic acid, whereas the iron salt loses acid and is oxidised to form a ferric compound. It is essential that the mordant be incorporated with the fibre in the ferrous state and be slowly oxidised while the acetic acid escapes, since ferric acetate cannot be fixed and is removed by the "dunging"-bath. According to Schlumberger the best results in dyeing are obtained if the iron is in a state of oxidation intermediate between ferrous and ferric oxide. An energetic and rapid oxidation by passing through oxidising agents, like chloride of lime or bichromate, would not yield good results. The oxidation is regulated and restrained within definite limits by adding certain oxidisable substances to the mordant. A solution of white arsenic in acetic acid, to which some glycerin is added, is used for this purpose. Such a solution is called *purple fixing liquor.*

Black liquor is sometimes mixed with red liquor to obtain chocolate shades, and in this case a salt of copper is added to the fixing liquor. It is difficult to fix the mordant when printing a mixture of iron and aluminium pyrolignite. Oscar Scheurer * has explained this circumstance by the fact that red liquor generally contains sulphates which form ferrous sulphate by double decomposition. Ferrous sulphate is a bad mordant, which leaves, on ageing, only a small amount of oxide on the fibre, whilst the same salt, with an addition of arsenic and a salt of copper, fixes much more. Scheurer has substituted, with good results, phosphoric acid for the arsenic.

The goods which have been mordanted with black liquor are passed, after ageing, through the dunging-bath in the same way as those treated with red liquor; cow-dung, arsenate, phosphate, or silicate of soda, &c., are used; all give good results.

(3) *Nitrate of Iron* is the most important ferric mordant used in cotton dyeing. A basic salt which holds an intermediate position between the normal salt, $Fe_2(SO_4)_3$, and the basic salt, $Fe_4(SO_4)_5(OH)_2$, is generally used. Basic ferric sulphate-nitrates of a similar composition are also frequently employed in cotton dyeing, as has been stated before.

The material may be mordanted by simply saturating it with nitrate of iron (3° to 6° Tw.), and subsequently passing it through a weak solution of caustic soda, soda ash, lime water, or chalk. The operations are repeated until enough ferric hydroxide is deposited in the fibre. In this way cotton is dyed iron-buff and blue (with prussiate). Another method is to prepare the material first with tannin (p. 189), and subsequently work and soak it for thirty to sixty minutes in a cold bath of nitrate of iron (2° to 4° Tw.). In this way an insoluble ferric tannate is produced in the fibre. To facilitate the formation of the salt by double decomposition it is advisable to previously pass the goods, after mordanting with tannin, through clear lime water, whereby calcium tannate is formed, and the formation of free acid in the iron liquor is prevented. A strongly caustic lye, however, would destroy the tannic acid. After the material has been steeped in the iron liquor, it is washed well in water to which a small quantity of chalk is added with advantage, since it pre-

* *Journ. Soc. Dyers and Col.*, 1887, p. 193.

cipitates the ferric hydroxide more completely in the fibre, and removes all free acid.

Goods which have been mordanted with ferric salts alone show a buff to brown colour; those mordanted with tannate of iron have a light brown or light grey to brownish-black or bluish-black appearance, the brown or blue being more decided according to whether the goods have been prepared with or without lime water. The dark colour prevents the application of iron mordant for light shades; in the production of dark colours tannate of iron serves partially as a mordant, partially as a self-colour, since it enables the dyer to produce full shades with relatively small amounts of colour.

Ferric Nitrate has a limited use in producing iron-buff and black shades. It is applied exactly like "nitrate of iron."

Jute is mordanted with copperas for blacks, the mordanting taking place after the impregnation with logwood extract.

Application to Wool.—*Ferrous sulphate* or *copperas* is practically the only iron salt which is used in wool dyeing. Formerly it was very extensively employed in dyeing logwood blacks, but since that time it has been replaced almost completely by potassium or sodium bichromate. It is employed in conjunction with logwood for the production of cheap blacks, which are required to be fast to light, the logwood blacks on chrome mordants being liable to turn green (see *Logwood*).

Ferrous sulphate has been used more frequently for the fixation of wood colours to produce brown shades. It is principally applied by the so-called *stuffing and saddening* method, the wool being boiled first with a decoction of the dyewoods for about one hour, and after addition of 5 to 8 per cent. copperas for one half hour more; sometimes a certain amount of sumach is added to the decoction of the woods to sadden the colour. Ferrous sulphate is also employed for darkening the shades of the Alizarins and other mordant colours by being added to the exhausted dye-bath, and the boiling being continued for fifteen to thirty minutes.

The application of ferrous sulphate by the *mordanting and dyeing* method is expensive, since comparatively large quantities of tartar or oxalic acid are required to produce good colours. With tartar in the mordanting-bath the wool receives a pale yellow colour, ferrous hydroxide probably being fixed by the fibre; without the addition of tartar a basic sulphate is precipitated in the fibre, which gives to the wool a deep reddish-brown colour.

Copperas also, if used by this method of dyeing, is generally combined with blue vitriol. The usual proportions are 15 to 20 per cent. copperas, 2 to 4 per cent. blue vitriol, and 3 to 5 per cent. tartar or oxalic acid. The mordanted wool is allowed to lie until the next day, the effect of mordanting being improved thereby.

For the production of Prussian blue on wool either yellow or red ferrocyanide of potassium, or a mixture of both, is used (see under *Mineral Colours*).

Application to Silk.*—Iron salts are very important materials for the production of black silk, both for mordanting and for weighting the goods (see *Black Dyeing of Silk* under the heading *Logwood*).

Ferrous Sulphate is not extensively employed for this purpose. It is used in silk dyeing for the production of the so-called "English black" (*noir anglais*) (see *Black Dyeing of Silk*).

Pyrolignite of Iron (*pied de fer*) is employed very extensively on raw silk, which has been previously prepared with tannin. The silk is first impregnated at 40° to 45° C. with a solution of tannic acid, generally in the form of chestnut extract; a quantity of extract standing at 15° Tw., equal to the weight of the silk, is used. After the silk has been saturated with tannic acid, it is worked

* See also P. Heermann, *l.c.*, p. 238.

for a short time at 50° to 60° in a liquor of pyrolignite of iron (about 13° to 15° Tw.), wrung and exposed to the air for half an hour, again passed through the iron liquor and hung up once more, and finally rinsed well in running water. The silk absorbs by this treatment 30 per cent. of its own weight, and in most cases has not yet received the desired weight or colour. By the treatment with pyrolignite it has become capable of absorbing a fresh quantity of tannin matter, and is now mordanted again with chestnut extract as before, but half as much more extract is used. The silk loses in appearance by the second tanning (but this is restored later by the iron mordant), and the fibre swells up. After the second tanning the silk is rinsed in running water, and then mordanted again in pyrolignite as before. It has now acquired a good bluish-black shade, and has taken up altogether 70 per cent. of its own weight. The weighting can be increased by one or more repetitions of the mordanting with tannin and iron to 130 or 200 per cent. The quality of the water is of great importance; if hard water is used the weighting is much more effective than in soft water, which latter necessitates a more frequent repetition of the operations.

The silk, which has lost its lustre by these operations, is now worked in a softening bath consisting of 30 to 40 per cent. white soap (of the weight of the silk) at the ordinary temperature, washed in running water, and then subjected to the brightening process. The brightening bath is prepared with sufficient hydrochloric acid to give a sour taste, and is used lukewarm. 6 to 12 per cent. of olive oil (in proportion to the weighting smaller or larger percentages) is added to the bath in a state of fine division, and the silk turned four to six times, wrung out, and dried at a low temperature. It has now regained its lustre, and acquired the peculiar crunching sound called the "scroop."

The pyrolignite bath is used continuously, and maintained at a strength of 13° to 15° Tw. by adding fresh liquor. The free acid which is liberated by the mordanting process is neutralised by adding iron filings to the bath and heating to incipient boiling; the scum which is formed thereby rises to the surface and is removed. The old method was always to have some iron filings in the bath, but a better plan is to hang a basket of iron filings in the upper part of the liquor from time to time, and to give the bath time to restore its neutrality by dissolving sufficient metal.

The bluish-black shade which the silk acquires by the treatment with ferrous salt cannot be obtained easily with ferric salts; oxidation seems to be an important factor, and if it proceeds too rapidly the colour is liable to be irregular.

For certain kinds of blacks a weak bath of pyrolignite is used between two tannin-baths for the sole purpose of improving the shade, not for weighting (see *Black Dyeing of Silk*).

Nitrate of Iron is used in large quantities for black dyeing and weighting of raw silk and boiled-off silk. Since silk which has been saturated with tannic acid becomes more or less impervious to ferric salts, and, in addition, tannic acid would be destroyed by the oxidising action of ferric nitrate in the mordanting-bath, the treatment with nitrate of iron precedes the tanning. A basic salt of the composition $Fe_4(SO_4)_5(OH)_2$ is most generally employed, as has been stated before, and this is readily dissociated, the silk attracting very considerable amounts of ferric hydroxide. Other ferric salts are employed in the same way. The mordanting of raw and boiled-off silk is essentially different.

Raw Silk is first worked in a tepid bath of sodium carbonate, washed and wrung out, and then worked in a cold bath of nitrate of iron at 15° Tw. After half an hour to an hour it is wrung out, well rinsed in running water, steeped for thirty minutes in a soda-bath (the temperature of which must not exceed

40° to 50°); and, finally, turned several times in cold water. This series of operations may be repeated two, three, or four times, according to the depth of colour and the amount of weighting required.

Boiled-off Silk is mordanted in a much stronger bath of nitrate of iron, 52° Tw. being the usual strength. The material, which has been well rinsed after being boiled off, is worked for half an hour to an hour in the iron liquor, washed in running water, wrung out, and worked for one hour in a boiling soap-bath to fix the ferric hydroxide. The soap-bath consists of boiled-off liquor, to which are added 12 per cent. of oleïn soap and 2 per cent. of soda crystals (of the weight of the silk); it is essential that it should be actually boiling. The soap-bath is used continuously, the liquor from the silk being allowed to run back, and each time fresh additions of soap and soda are made; after each operation the bath is boiled up again in order that the iron soap formed may rise to the surface and be skimmed off. The silk which has been drained into the soap-bath is washed, first in a tepid soda solution, then in running water, and finally wrung. It has now acquired a brown colour, whereas it was pale yellow when it came from the iron liquor. The series of operations can now be repeated seven to eight times if necessary. As the silk is liable to be tendered by ferric salts on drying in the air, the material should not be allowed to dry when charged with the mordant; if it cannot be worked up directly, it is left in the mordanting-bath or well covered up with wet sheets.

The nitrate of iron baths are permanent, and the liquor which is drained from the silk is returned as completely as possible, since, in spite of the low price, the expense for nitrate of iron is considerable. The specific gravity of the baths is carefully maintained at the same degree by additions of fresh liquor.

Raw silk seems to possess a strong affinity for iron salts, since it takes up a large quantity from comparatively weak solutions; the subsequent rinsing in water completes the dissociation, and removes the liberated acid salt before the basic salt is fixed by the soda-bath.

Boiled-off silk shows no affinity for the iron salts. The mordant is simply absorbed by the fibre and dissociated into a basic salt, which is precipitated in an insoluble state in the fibre, and an acid salt which is washed out; by systematic washing nearly all the iron salt can be removed, according to Moyret (*l.c.*). Hard water is much better for the washing of boiled-off silk in this phase of mordanting, since it fixes greater quantities of iron. Whereas the raw silk binds the mordant chemically, in the boiled-off silk it is simply deposited, and liable to dissolve in the following iron liquor-baths. To prevent this it is subjected to the high temperature of the boiling soap-bath, whereby it is converted into a less soluble hydroxide; an iron soap is not formed in this case.

By each operation of mordanting with nitrate of iron the raw or discharged silk increases about 4 per cent. in weight; it acquires thus a deep brown colour and loses none of its lustre.

The washing of the mordanted silk is generally done with the aid of specially constructed washing machines (see *Machinery*).

The weighting of silk with ferric oxide for black-dyeing is frequently followed by a treatment with ferrocyanide of potassium to produce Prussian blue. This treatment weights the silk still further, but it also produces a dark navy-blue bottom which yields a fuller and finer black than can be otherwise obtained. In addition the silk is better disposed to take up tannin-substances after the blue dyeing.

Raw silk and boiled-off silk are again treated in different ways, since they contain the oxide of iron forming the basis of the Prussian blue in a different

state. Raw silk offers the oxide in a form which combines easily with the ferrocyanide, whereas the ferric oxide which has been precipitated by a hot soap-bath in the boiled-off silk is not easily affected and requires a higher temperature. About 10 to 20 per cent. of yellow prussiate of potash are used for each bath, in proportion to the weighting with oxide of iron which the silk has received previously; an excess is not injurious. In addition, a quantity of hydrochloric acid equal to the prussiate is required. An excess of acid may decompose the prussiate, as is indicated by the intensely blue turbidity of the bath; it is also injurious to the fibre, and the blue is not fixed well.

Raw silk is first placed in the bath which has been prepared with the prussiate and with about one-half of the hydrochloric acid required at 30° to 35° C. The silk is worked for half an hour in the bath and then lifted so as to allow of the rest of the acid being added, while the temperature is raised to 40°. The material is then replaced in the bath and worked as before, wrung out, and washed in fresh water. It is then ready for the following dyeing and weighting operations, and has a blue, almost black, colour, the depth of which depends on the quantity of ferric oxide already fixed.

Boiled-off silk is treated at a higher temperature in order to cause the ferric oxide to combine with the ferrocyanide; otherwise the process is precisely similar. Enter at 30° C., turn the silk about ten times, heat to 45°, turn a few times, add the other half of the acid and heat to 50° to 55°, turn again a few times, wring out and wash well in water. The dyeing should take not less than thirty minutes; the temperature may be carried to 60°, but not higher.

The baths of yellow prussiate are not used continuously—neither for raw nor for boiled-off silk. They are thrown out each time; if the right quantities are employed, they are nearly exhausted. In the same bath only such lots of silk should be dyed as have been prepared with nearly the same quantities of ferric oxide—*i.e.*, those which have passed through nearly the same number of mordanting operations.

TIN (*Stannum*), Sn = 119.

Tin is di- and tetravalent. It forms a bluish-white metal of 7·3 specific gravity, which melts at 235°, and volatilises at a strong white heat. It is soft, malleable, and ductile, but not very tenacious, and possesses a crystalline structure. Tin does not lose its lustre in the atmosphere; when heated strongly it takes fire and forms stannic oxide (SnO_2). It dissolves in strong hydrochloric acid with evolution of hydrogen, forming stannous chloride ($SnCl_2$); the metal is attacked with great energy by strong nitric acid, nitrous gases being given off and stannic oxide formed. Tin is frequently employed, in consequence of its not being easily attacked, as a lining for dye-vats, especially for cochineal scarlets on wool and in silk dyeing.

Tin combines in two proportions with oxygen to form—

(1) Stannous Oxide or Tin Monoxide (SnO).
(2) Stannic Oxide or Tin Dioxide (SnO_2).

Stannous Oxide, SnO, is a black powder that rapidly absorbs oxygen; it is prepared by heating stannous hydroxide in a current of carbon dioxide.

Stannous Hydroxide, $Sn(OH)_2$, is obtained as a white powder on adding an alkaline carbonate to the solution of a stannous salt. It is soluble in caustic potash or caustic soda, not in ammonia. Stannous hydroxide is a weak base and a weak acid. The salts in which it acts as a base are called ***stannous salts***, those in which it acts as an acid ***stannites***. On boiling a solution of stannite of sodium tin is thrown down and sodium stannate formed; but, if it is slowly evaporated, stannous oxide is deposited.

Stannous salts are produced by dissolving metallic tin or stannous hydroxide in acids; they are colourless, and are mostly decomposed by high temperatures. Those which are soluble in water redden blue litmus and have a disagreeable metallic taste. They absorb oxygen from the air and are strong reducing agents. Sulphuretted hydrogen precipitates from the acid and neutral solutions dark brown stannous sulphide, which is soluble in caustic potash or soda and in the alkaline polysulphides.

Stannic Oxide, SnO_2, occurs native as tin stone, and can be prepared, by heating tin in a current of air, as a white powder, which is insoluble in acids and solutions of the alkalies; when melted with caustic soda, it forms stannate of soda. Two *stannic hydroxides* of totally different properties are known—*stannic hydroxide* or stannic acid and *metastannic acid.*

Stannic Hydroxide or Stannic Acid, H_2SnO_3, is obtained as a white precipitate by adding ammonia to the solution of a stannic salt or an acid to a solution of stannate of soda. It is slightly soluble in water and reddens blue litmus; it dissolves readily in hydrochloric, nitric, and sulphuric acids, in caustic potash and caustic soda; it is both a weak acid and a weak base, the acid character being prevalent. The salts in which it acts as an acid are called *stannates,* the most important of which is stannate of soda (see below). The soluble stannates have a strong alkaline reaction, and are decomposed even by the carbonic acid of the air, stannic hydroxide being separated. The salts in which stannic hydroxide acts as a base are called *stannic salts.* They are colourless. Those which are soluble in water have an acid reaction, a disagreeable metallic taste, and are decomposed by strong heat. Sulphuretted hydrogen precipitates from acid and neutral solutions of stannic salts yellow stannic sulphide, which is soluble in alkaline sulphides. Most of the neutral salts of the alkalies, notably sodium sulphate and ammonium nitrate, precipitate stannic hydroxide from the aqueous solutions, unless a great amount of acid be present in the free state.

Metastannic Acid, H_2SnO_3 (?), or $H_{10}Sn_5O_{15}$ (?), is obtained by heating tin in concentrated nitric acid as a white powder, which is not readily soluble in acids or in alkalies. It is both a weak acid and a weak base. It is formed wherever tin is violently acted upon by nitric acid—*i.e.,* when the latter is too concentrated or the temperature employed too high. The formation of metastannic acid during the preparation of tin mordants is called "firing"; it must be avoided, since this substance has no mordanting power and its generation involves loss of tin.*

Stannous Chloride, $SnCl_2$ **(Tin Crystals or Tin Salt,** $SnCl_2 + 2H_2O$**).**—This salt is prepared by dissolving tin in hot hydrochloric acid; it forms in the anhydrous state a white transparent mass which melts at 250° and can be distilled without being decomposed. From the aqueous solution monoclinic crystals are obtained which contain two molecules of water of crystallisation ($SnCl_2 + 2H_2O$) and which are known commmercially as *tin crystals.*

Stannous chloride in the crystalline form dissolves with absorption of heat and is soluble in 0·37 part of water. The clear solution becomes turbid on dilution with water, insoluble basic stannous chloride or oxychloride being separated by dissociation—$SnCl_2 + H_2O = SnCl(OH) + HCl$. The same precipitate is produced by the action of the air on the clear solution—$3SnCl_2 + H_2O + O = 2SnCl(OH) + SnCl_4$.

Tin crystals are oxidised in the same way by exposure to the air. The basic chloride redissolves on addition of hydrochloric acid.

Stannous chloride dissolves readily in alcohol, and forms crystalline double salts with the alkaline chlorides. Solutions of stannous chloride which have

* As to the detection of metastannic acid, see H. Bayerlein, Lehne's *Färber Zeitung,* 1907, p. 241.

been prepared by dissolving tin in hydrochloric acid without crystallising are sold under the names *single muriate of tin* and *double muriate of tin*, according to their lower or higher specific gravity (60° to 120° Tw.). Their composition varies; owing to an excess of acid they are less prone to dissociate than tin crystals.

Stannous Sulphate, $SnSO_4$, is obtained by dissolving tin or stannous hydroxide in diluted sulphuric acid. The solution yields minute, granular, and very soluble crystals, and is dissociated by diluting with water.

Stannous Nitrate, $Sn(NO_3)_2$, is known in solution only. It is obtained by dissolving tin or stannous hydroxide in diluted nitric acid. In the former case ammonium nitrate is formed—

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

Stannous nitrate is usually prepared by dissolving tin in form of bars (grain bar tin)—not granulated tin—in eight times their weight of nitric acid (32° Tw.); the acid must be free from the lower oxides of nitrogen. Care is taken, by adding the tin bars slowly and keeping the acid cool, that no nitrous gases are given off; if the reaction becomes violent the mass is liable to "fire," metastannic acid being formed, which has no mordanting properties. The deep yellow solution of about 60° Tw. becomes turbid in the air, and deposits a white precipitate on long standing

Woollen dyers use stannous nitrate in the production of cochineal scarlets under the names of *nitrate of tin*, *scarlet spirits*, *bowl spirits.*

Tin Spirits is a general term in the dyeing trade, given to a great variety of solutions of tin, in the preparation of which other acids besides hydrochloric acid, notably sulphuric, nitric, and oxalic acids, are used; along with these acids some salts, *e.g.*, nitrate of soda, salammoniac or common salt are employed, the utility of which often appears doubtful. They are chiefly used in wool dyeing in the production of certain colours with the natural colouring matters, and are largely prepared by the dyers themselves, who have their own peculiar recipes, on the virtue of which they believe their success depends. The value must be determined by a practical dye-trial. See also *Cotton Spirits*, p. 275. Since the introduction of the artificial dyestuffs these tin spirits have lost their former importance.

Yellow, Orange, Scarlet, Red, Amaranth, Purple, Plum, Puce Spirit, Aniline Spirit, Scarlet Finishing Spirit, and the like are all prepared by dissolving tin in mixtures of hydrochloric, sulphuric, nitric, and other acids, or by adding one or several of these acids to the solution of stannous chloride.

The difference in the value of these mixtures is greatly imaginary, and the better results which some dyers obtain with their peculiar preparations are more due to the care and experience in making them than to the nature of the acids. The state of oxidation in which the tin is dissolved is of prime importance; for woollen dyeing the stannous salts are best, whereas in cotton and silk dyeing the stannic salts are chiefly employed.

Stannous Acetate, $Sn(C_2H_3O_2)_2$, is prepared by the double decomposition of a solution of tin crystals, acidulated with acetic acid, and lead acetate. The colourless solution, which dissociates readily both on gentle heating and on diluting, is employed in calico-printing.

Stannous Oxalate, SnC_2O_4, is obtained as a white crystalline powder on addition of oxalic acid to solutions of stannous chloride. It is soluble in the solutions of alkaline oxalates, forming double salts. In mordanting wool with a mixture of stannous chloride and oxalic acid the precipitate which forms at first disappears. Under the name of *oxalate of tin*, mixtures of tin spirits containing oxalic acid are sometimes sold.

Stannous Tartrate, $Sn(C_4H_4O_6)$, has scarcely been studied. Stannous

hydroxide is only sparingly soluble in tartaric acid, but dissolves easily in tartar. Stannous tartrate is rapidly dissociated by heat and by water; it is not a good wool mordant.

Stannic Chloride, $SnCl_4$ (*Oxymuriate of Tin*).—In the anhydrous state the salt is obtained by passing a current of chlorine gas over heated tin foil; it is a colourless liquid, which boils at 120°, and does not become solid at − 29°. It fumes strongly in the air and combines with water, forming several crystalline hydrates which are very soluble in water—$SnCl_4 + 3H_2O$; $SnCl_4 + 5H_2O$; $SnCl_4 + 8H_2O$. Stannic chloride is prepared on the large scale by the oxidation of solutions of stannous chloride with chlorine gas or nitric acid, or chlorate of potash—

$$SnCl_2 + Cl_2 = SnCl_4.$$
$$3SnCl_2 + 6HCl + 2HNO_3 = 3SnCl_4 + 2NO + 4H_2O.$$
$$3SnCl_2 + 6HCl + KClO_3 = 3SnCl_4 + KCl + 3H_2O.$$

Tin crystals are dissolved, for example, in hydrochloric acid and boiling water, and potassium chlorate is added until the colourless solution becomes yellowish, and smells of chlorine. The reaction must not become too vehement, else insoluble metastannic acid is formed. For 1 kg. (10 lbs.) of dry crystals ($SnCl_2 + 2H_2O$) there are required about 1,300 grms. (13 lbs.) of hydrochloric acid (25° Tw.), 3½ litres (3½ galls.) of boiling water, and 1,800 grms. (18 lbs.) of potassium chlorate. With a deficiency of hydrochloric acid the solution becomes turbid; if the slight excess of chlorine has not disappeared after the liquor has become cold, it is neutralised with a little stannous chloride. About 1,500 grms. (15 lbs.) of $SnCl_4 + 5H_2O$ are obtained; if an insufficient quantity of water is used crystals of a double salt of stannic chloride and potassium chloride will form. Anhydrous stannic chloride is now manufactured by the action of chlorine gas on tin-plate waste. The product is a colourless liquid of 2·26 specific gravity and contains 45·4 per cent. of tin. It is free from iron, lead, nitrates, sulphates, stannous chloride, metastannic acid, salt, free acid and free chlorine.*

Stannic chloride is sold in monoclinic crystals, $SnCl_4 + 5H_2O$, or as an aqueous solution. The following table gives the specific gravity and strength of solutions of pure stannic chloride ($SnCl_4 + 5H_2O$) at 15°, according to Gerlach:—

Specific Gravity.	Per Cent. $SnCl_4+5H_2O$.	Specific Gravity.	Per Cent. $SnCl_4+5H_2O$.	Specific Gravity.	Per Cent. $SnCl_4+5H_2O$.
1·012	2	1·227	34	1·538	66
1·024	4	1·242	36	1·563	68
1·036	6	1·259	38	1·587	70
1·048	8	1·276	40	1·614	72
1·059	10	1·293	42	1·641	74
1·072	12	1·310	44	1·669	76
1·084	14	1·329	46	1·698	78
1·097	16	1·347	48	1·727	80
1·110	18	1·366	50	1·759	82
1·124	20	1·386	52	1·791	84
1·137	22	1·406	54	1·824	86
1·151	24	1·426	56	1·859	88
1·165	26	1·447	58	1·893	90
1·180	28	1·468	60	1·932	92
1·195	30	1·491	62	1·969	94
1·210	32	1·514	64	1·988	96

* P. Heermann, *Färber Zeitung*, 1907, p. 34.

The following table of the specific gravity and strength of solutions of pure stannic chloride has recently been published by P. Heermann (*Chemiker Zeitung*, 1907, p. 680).

° Bé.	Per Cent. Sn.	° Bé.	Per Cent. Sn.	° Bé.	Per Cent Sn.	° Bé.	Per Cent. Sn.
65·7	29·45	58	25·84	50	22·20	32	14·00
65	29·12	57	25·38	49	21·74	31	13·56
64	28·64	56	24·93	48	21·29	30	13·11
63	28·17	55	24·47	47	20·83	29	12·67
62	27·70	54	24·02	46	20·38	28	12·23
61	27·24	53	23·56	...	...	27	11·79
60	26·77	52	23·11	34	14·90	26	11·35
59	26·30	51	22·65	33	14·45	25	10·91

The tables of Gerlaeh and Heermann agree well with each other.

Diluted solutions of stannic chloride dissociate on long standing only; on boiling, stannic hydroxide is precipitated at once—

$$SnCl_4 + 3H_2O = SnO_3H_2 + 4HCl.$$

Stannic chloride combines with many chlorides, forming crystalline compounds—*e.g.*, $SnCl_4 + 2SCl_4$ and $SnCl_4 + PCl_5$. With the chlorides of the alkali metals it forms crystallised double salts.

Stannic chloride is an important mordant for cotton and silk.

Pink Salt, $SnCl_4 + 2NH_4Cl$, is the double salt of stannic chloride and ammonium chloride.* It crystallises from the solution of a mixture of the salts in small regular octahedra which are stable in the air and dissolve in 3 parts of water. The concentrated solution of the salt can be boiled without decomposition; the diluted solution separates stannic hydroxide on boiling.

Pink salt was largely used as a mordant in former years, but it has been replaced almost entirely by stannic chloride.

Stannic Nitrate and **Stannic Sulphate** have been but little studied. Stannic hydroxide dissolves both in nitric and in sulphuric acid. Stannic sulphate remains as a white mass on evaporating the aqueous solution; the solution of stannic nitrate coagulates at 50°.

Cotton Spirits or **Tin Spirits** are also general terms for solutions of tin salts used as mordants for cotton. We refer to what was said on p. 273. The cotton spirits consist chiefly of stannic salts, whereas the previously mentioned tin spirits are principally stannous salts. There exists, however, a great amount of confusion as to the names. These preparations have also lost much of their importance since the introduction of the artificial dyestuffs. They are prepared by the dyers themselves in various ways so as to produce mixtures of stannous and stannic chloride and nitrate; for 1 to 2 parts of tin 8 to 16 parts of nitric acid and 8 to 50 parts of hydrochloric acid are employed; ammonium chloride, bichromate of potash, and other salts are also added.

Crimson, *Barwood*, *Plum*, *Red Cotton*, *Purple Cotton Spirit*, *Solution of Tin*, or simply "*Solution*" and *Pink Cutting Liquor* are some of the usual names.

Stannic Sulphocyanide or Thiocyanate, $Sn(CNS)_4$, is obtained by the double decomposition of stannic oxalate (see below) and calcium sulphocyanide, or by dissolving stannic hydroxide in sulphuric acid, and decomposing the solution with barium sulphocyanide. The diluted solution can be boiled without decomposition. Stannic sulphocyanide is used in calico-printing.

* Crystallised stannic chloride, $SnCl_4 + 5H_2O$, is also found in commerce under the name of "pink salt."

Stannic Acetate, $Sn(C_2H_3O_2)_4$, is obtained by mixing strong solutions of stannic chloride and sugar of lead with the addition of some acetic acid. The solution, which is used in the production of certain steam colours on calico, is not dissociated by boiling if it contains sufficient acetic acid—about 1 part acetic acid to 2 parts of crystallised acetate of lead is required.

Stannic Oxalate, $Sn(C_2O_4)_2$—*Oxalate of tin*—is prepared by dissolving stannic hydroxide in a solution of oxalic acid on the water-bath at 65° to 80°. The salt dissolves in much water; the solution becomes opalescent in the air. Stannic oxalate is also used in calico-printing for the production of Alizarin reds and similar colours.

Stannic Tartrate, $Sn(C_4H_4O_6)_2$.—Stannic hydroxide dissolves in a solution of tartaric acid. The compound has not yet been exactly described.

Sodium Stannate, Na_2SnO_3—*Stannate of Soda; Preparing Salt.*—Sodium stannate is obtained by melting tin-stone (stannic oxide, SnO_2) with caustic soda or tin with sodium nitrate and caustic soda. The commercial product contains sodium chloride and carbonate; sodium arsenate and sodium tungstate are sometimes added to increase the effect of the salt.

Sodium stannate is a white crystalline mass, readily soluble in water. It forms crystals with 3 and 10 molecules of water. Stannic acid being a very weak acid, the salt has mild caustic properties. It is slowly decomposed by atmospheric carbon dioxide with formation of sodium carbonate and stannic acid, H_2SnO_3. Sodium stannate is used in dyeing and in printing as a mordant (see pp. 277 and 278).

APPLICATION OF THE COMPOUNDS OF TIN TO THE TEXTILE FIBRES.

The compounds of tin are used by dyers almost exclusively as mordants. The colours they yield are distinguished, as a rule, by their brilliancy. Apart from their employment as mordants, the stannous salts are used in calico-printing as resists and discharges. The stannous salts attract oxygen with great avidity, and their application in resists and discharges is based on their reducing properties. The reducing power prohibits the stannous salt from being used in conjunction with oxidising mordants, or with colouring matters which are decolourised by reducing agents. The most important application, however, is now that of the stannic salts for weighting silk, for which purpose immense quantities of stannic chloride are used.

Application to Cotton and Linen.—*Stannous salts* are not frequently employed as mordants on cotton and linen. Persian berries yield a good yellow to orange shade on these materials previously mordanted with tannin and stannous chloride, and Soluble blue is faster to light on material thus prepared than on tannin and antimony mordant. Certain lakes which are produced by means of stannous chloride and various extracts are sold under the name of *carmines*—*e.g.*, Persian berry carmine, cochineal-carmine, &c.—and are used in cotton dyeing and calico-printing. In Turkey-red dyeing stannous chloride is added in very small quantities to the clearing bath; whether it exerts in this case simply a reducing influence, or enters into the colour lake as a mordant proper, has not been definitely decided.

Stannous chloride both reduces ferric salts and eventually converts them by double decomposition into chlorides, which do not readily dissociate, and are not easily fixed on the fibre. For this reason stannous chloride is sometimes added to print colours, notably to Alizarin reds, to preserve their brilliancy in the presence of ferruginous impurities.

Stannic salts are extensively used as mordants for cotton and linen. Many natural dyestuffs—*e.g.*, logwood, fustic, quercitron, weld, barwood, &c.—are

fixed on these fibres with stannic oxide. The cotton spirits which have been mentioned above are still used for this purpose, and were formerly employed in large quantities. Generally the material is first mordanted in tannin, then worked and soaked in a diluted liquor of stannic chloride or spirits, &c., and, finally, well washed before dyeing. In these cases tannic acid acts as a fixing agent for stannic hydroxide, which is the actual mordant. The inverse takes place with the Aniline colours, which are also frequently dyed on tannic acid and stannic oxide, &c. (stannic tannate), the basic dyestuffs being bound to the fibre by tannic acid, while the stannic oxide simply serves to precipitate the tannic acid as an insoluble salt. An excess of tannic acid, if not converted into an insoluble salt, would redissolve the ultimate colour lake (see p. 189). When tannin is thus fixed on cotton by means of stannic chloride, in dyeing cotton and wool mixed goods, the salt should be free from stannous salt, since the wool is liable to be mordanted by the latter.

Stannate of soda is employed as a mordant on the vegetable fibres for the same purposes as the stannic salts to fix the natural colouring matters, but it is applied differently on account of its opposite chemical character. The goods are simply impregnated with a solution of stannate of soda (4° to 10° Tw.) and then passed through very dilute sulphuric acid, or normal or basic sulphate of alumina. Stannic hydroxide, or, in the latter case, a mixture of stannic hydroxide and aluminium hydroxide, are precipitated in the fibre. This mordant also serves well for the Eosins and for many azo-colours.

Cotton piece goods are sometimes prepared with tin by running them through stannate of soda and then through sulphuric acid; brighter and richer colours are obtained in this way, especially in printing.

Application to Wool.—The tin mordant of the woollen dyer is principally stannous chloride, often in the form of the tin spirits already referred to. The best method is to mordant with about 4 per cent. stannous chloride and 2 per cent. oxalic acid (of the weight of the wool) at the boil; tartar does not give such good results as oxalic acid. A mixture of equivalent amounts of stannous and stannic salt, as contained in many tin spirits, also gives good shades; it is, however, subject to deterioration. An excess of tin mordant makes the wool harsh and rough, and destroys its milling properties. The wool is entered into the cold mordanting bath, the temperature gradually raised to boiling, and kept at this temperature for one hour. Oxalic acid first precipitates stannous oxalate, and the salt is slowly taken up by the fibre during the mordanting process.

Liechti and Schwitzer * have studied the behaviour of tin mordants towards wool. Stannous tartrate and stannic tartrate are not good mordants for wool, since they are too prone to dissociation. As is the case with aluminium, tin salts require an acid in the mordanting bath to prevent a premature dissociation and superficial fixing of the mordant. Stannous chloride and tartar give the best results in the proportions of 4 per cent. tin crystals and 3·2 per cent. tartar—*i.e.*, equal molecules. Better effects, however, are obtained by using 4 per cent. tin crystals and 2·1 per cent. oxalic acid (equal molecules), which mordant is besides preferable on account of its lower cost. Tartaric acid in the free state gives slightly better results than oxalic acid, but is not worth the greater expense involved by its use. A mixture of one equivalent of stannous and one equivalent of stannic salts gives very good results, and in this case oxalic acid is again the most satisfactory assistant; three equivalents or slightly greater quantities of the latter are required to obtain a colour fast to rubbing. This mixed mordant has the disadvantage of deteriorating on standing for a long time. In the case of mordanting with sulphate of aluminium and a tin salt Liechti and Schwitzer maintain that

* *Journ. Soc. Dyers and Col.*, 1886, p. 177; 1887, pp. 25 and 44.

it is best to employ stannous chloride along with tartar. Colours produced with this mordant have the advantage of not rubbing. According to the same authors, dye-trials with cochineal proved that in mordanting with stannous salts considerably more acid is taken up by the wool fibre than with stannic salts. With some colouring matters, especially with cochineal and Flavin, no separate mordanting and dyeing is required, since the tin lakes which are formed at first are slowly taken up by the wool fibre.

The dye-bath is prepared with the dyestuff, stannous chloride, and oxalic acid, tartar, &c., and the wool dyed by the so-called single-bath process.

Stannous chloride is added to the logwood dye-bath in certain cases towards the end of the dyeing process to shade the colour by making it more brilliant; this operation is called "blooming."

In woollen printing the cloth is sometimes prepared with stannate of soda in a similar manner to that mentioned for calico. The woollen cloth is padded twice in stannate of soda (16° Tw.), and then passed through dilute sulphuric acid. The usual chlorination follows.

Application to Silk.—*Stannous chloride* is employed in conjunction with catechu to produce heavily weighted blacks on a bottom of ferric oxide or Prussian blue (see *Catechu* and *Logwood*).

Stannic chloride in form of tin spirits has been used in the dyeing with the natural colouring matters; but such application has become rare since the introduction of the artificial dyestuffs.

Stannic chloride is now used in very great quantities for the weighting of white or light-coloured as well as black silk. The silk is generally used in the raw state, since it would have to be soaped again after being mordanted.*

The older method is to steep the material in a solution of stannic chloride (32° to 52° Tw.) until it has become thoroughly impregnated with the solution. (The liquor is kept in a stone vat.) The fixation of the tin may be effected by merely dissociating the stannic chloride with water. For this purpose the well-saturated silk is wrung out, and the excess of liquor returned to the bath, the silk is then rinsed in running water to precipitate stannic hydroxide in the fibre, while a soluble acid salt is removed by washing. Frequently a cold solution of soda is used for the fixation. The weight of the silk can be increased up to 25 per cent. by repeated operations. The solution of stannic chloride must not be too strong, since the silk shrinks perceptibly in a solution of the salt at 50° Tw., and begins to dissolve in a liquor at 100° Tw. Repeated soapings at the boil are necessary to restore the natural feel to the silk, and it is always prone to deteriorate after some time under the influence of light. The tin has also an injurious effect on some of the colours which are afterwards applied. If these colours are not dulled too much by such treatment the silk is often weighted first with stannic chloride, and, subsequently, with tannin (tannic acid, sumach, or catechu) in order to prevent the subsequent deterioration of the fibre and to increase its weight and volume.

More recently this method has been improved by the use of phosphate of soda, the silk, after steeping in the stannic chloride and rinsing in water, being worked thirty minutes at 50° to 60° C. and thirty minutes at the boil in a solution of the phosphate, and then well rinsed. The treatment in stannic chloride and phosphate of soda is repeated séveral times, sufficient sulphuric acid being added to the last bath of phosphate to liberate one-third of the phosphoric acid employed. This treatment is less detrimental to the silk than the former, and yields a higher weighting. As the subsequent tanning is unnecessary, the white colour, the gloss, and the feel of the silk are much better preserved.

A further improvement was patented by J. H. Neuhaus' successor of

* See also the very exact researches of P. Heermann, *l.c.*, p. 238.

Crefeld, by the application of sodium silicate, which yields a weighting of 50 to 60 per cent., and even 100 to 120 per cent., above "pari" without injuring the gloss and feel of the fibre, although, after some time, a considerable weakening of the fibre is sometimes observed. Neuhaus treats the silk for one hour in stannic chloride (42° to 52° Tw.), and after squeezing and rinsing for one-half to one hour in a warm bath of soluble phosphates—*e.g.*, sodium phosphate (4° to 7° Tw.)—the silk is then again rinsed, worked for one-half to one hour in a warm bath of sodium silicate (4° to 7° Tw.), and eventually rinsed. The silk is weighted to 100 to 120 per cent. above "pari" by five passages through stannic chloride, sodium phosphate, and silicate. The treatment with silicate renders the silk somewhat hard, and, therefore, it is usually dispensed with after the first, and even the later, treatments with phosphate, and applied only for the third and following ones. Some of the treatments with phosphate are occasionally omitted. Gnehm and Baenziger,* who studied this process very thoroughly, give the following scheme:—Tin, phosphate, tin, phosphate, tin, phosphate, tin, phosphate, tin, silicate, tin, silicate, whereby a weighting of 120 to 150 per cent. above "pari" was attained. E. C. Puller found that the weighting is increased by 19 per cent. by treating the silk between the phosphate- and the silicate-baths in aluminium sulphate (15° Tw.). Other metallic salts have been recommended for the same purpose.

The baths of stannic chloride become strongly acid by continued use, more stannic oxide than acid being taken up by the silk. For restoring their original strength, in addition to stannic chloride, some ammonia must be added to the baths to keep them in good condition. The quantity of ammonia required is determined by a preliminary test. After some time the liquor will contain too much ammonium chloride, and must be let off; the tin is recovered by precipitating with lime and reducing to metal.†

Excessive weighting of silk by the tin-phosphate-silicate process is liable to bring about serious faults in the goods. Thus, silk heavily weighted by this process has frequently been found to become quite tender by a comparatively short exposure to direct sunlight. On the other hand, reddish-coloured spots often appear in the pieces, but are sometimes only found after the latter have been stored for months. Where these spots have formed the silk is usually tender. Gnehm, Roth, and Thomann ‡ attributed their formation to the action of perspiration. Later on, Sisley § showed that the only constituent of the latter which had an injurious action was the salt. More recently, O. Meister ‖ pointed out that the destruction of the fibre was due to active chlorine produced by the catalytic action of copper, which was always found to be present, though in very small quantities, and gets into the goods by careless handling during spinning and weaving. This author has suggested padding the goods in a weak solution of ammonium sulphocyanide as a preventive. Though this treatment has been found effective to a considerable extent, it is not infallible. Still more recently the use of thio-urea¶ and its salts and derivatives has been patented for the same purpose.

It is said that silk which has been weighted by the tin-phosphate process, and has subsequently become tender, regains its strength on being treated with hydrofluoric acid.

TITANIUM, Ti = 48·1.

This metal, which has until comparatively recently been classed among the rarer elements, occurs in nature both widely distributed and in large quantities.

* *Journ. Soc. Dyers and Col.*, 1897, p. 40.
† *Ibid.*, 1889, p. 159.
‡ *Ibid.*, 1902, p. 256.
§ *Ibid.*, 1902, p. 276.
‖ *Ibid.*, 1905, p. 192.
¶ *Ibid.*, 1907, p. 51.

The metal itself is difficult to prepare in the pure state, and has no technical interest. It yields, altogether, four oxides, and of these the salts of two only —viz., Ti_2O_3 and TiO_2—are articles of commerce. The sesquioxide Ti_2O_3 is obtained in the form of its hydrate by the addition of a caustic alkali to titanous sulphate as a black precipitate which readily absorbs oxygen from the air, yielding the white TiO_2. So great is its affinity for oxygen that even at the ordinary temperature, but more readily on warming, it decomposes water with liberation of hydrogen—$Ti_2O_3 + H_2O = 2TiO_2 + H_2$. The sesquioxide and its salts are very powerful reducing agents.

Titanous chloride * (Titanium trichloride or sesquichloride), $TiCl_3 + 6H_2O$. This salt can be obtained by the reduction of titanic chloride by means of zinc, tin, aluminium, &c., or by electrolysis. It crystallises from its very concentrated solution in violet crystals which rapidly absorb oxygen from the air, even when dry; the solid is, consequently, not a commercial article. Titanous chloride is sold as a violet-coloured solution containing 20 per cent. $TiCl_3$, along with an excess of free hydrochloric acid. The solution can be diluted with water to any extent as long as the latter does not contain any temporary hardness or alkalinity. In case only hard water should be available, the titanous chloride should be mixed, before being diluted, with an equal volume of hydrochloric acid.

Titanous sulphate, $Ti_2(SO_4)_3$, can be obtained in solution by the electrolytic reduction of titanic sulphate, and is sold like the chloride, as a 20 per cent. solution. With sodium sulphate it forms double salts, one of which can be obtained by salting out its deep purple black solution at the boil. It has the composition $Ti_2(SO_4)_3 . Na_2SO_4 . 5H_2O$, and crystallises in lilac-coloured cubes, readily soluble in water. A more hydrated form, having the composition $Ti_2(SO_4)_3 . Na_2SO_4 . 12H_2O$, forms much larger crystals, and is much less stable in the air.

Titanous fluoride can be obtained by the reduction of titanic fluoride, and dissolves in water with a violet colour, while its double compound with sodium fluoride is green. The oxalate and the double compound titanous potassium oxalate are brown and yellow in colour respectively; the latter is very sparingly soluble in water.

The titanous salts are characterised by their powerful reducing properties; they are, in fact, the most powerful acid-reducing agents that are technically available. Titanous chloride reduces ferric salts quantitatively in the cold, and, on boiling, acts similarly on nitro- and nitroso-compounds, azo dyes, and most of the colouring matters which yield leuco-compounds. In view of its powerful reducing action, it is noteworthy that it does not reduce mercuric chloride in the cold. Titanous sulphate behaves in most cases like the chloride, but differs from this in its behaviour towards copper sulphate, from which it throws down the whole of the copper as metal; whereas, in the case of the chloride, only a portion of the metal is thrown down, the reaction being apparently a reversible one. The reaction of the sulphate with copper sulphate is sufficiently delicate to serve as a means of detecting the presence of copper in the ash of dyed fabrics.

Titanic sulphate, $Ti(SO_4)_2 + 3H_2O$, is formed by dissolving titanic hydrate in cold sulphuric acid, but is not easily obtained in a crystalline form. The double compound with sodium sulphate, having the formula $Ti(SO_4)_2 + Na_2SO_4 + 2H_2O$, is, however, readily obtained in the form of well-defined needle-shaped crystals, and is a commercial article. It dissolves in a little over a third of its weight of cold water, but the solution only takes place slowly. If the water

* The true titanous chloride, $TiCl_2$, corresponding to stannous chloride can only be obtained with difficulty—*e.g.*, by passing hydrogen over the trichloride heated to redness in a porcelain tube. It has no technical importance.

is heated the compound decomposes, and then only goes into solution after standing in the cold for a very long time.

Titanic potassium oxalate, $TiOC_2H_4 + K_2C_2O_4 + H_2O$, forms well-defined crystals, readily soluble in hot water, and is the most stable of the crystallised titanic salts. It is a commercial article, and finds considerable application in the leather industry.

Titanium tanno-oxalate is a solution of titanium tannate in oxalic acid. It is of a deep brown colour, and finds application in the dyeing of chrome tanned and alumed leathers, and also of cotton.

The titanic salts are characterised by their behaviour towards peroxide of hydrogen and towards tannic acid. With the former they yield an intense orange to yellow colouration, the reaction constituting a very delicate test for either titanic compounds or peroxide of hydrogen. With tannic acid insoluble titanic tannate is produced, which also has an orange colour.

APPLICATION OF THE TITANIUM COMPOUNDS TO THE TEXTILE FIBRES.

Cotton and Linen.—Cotton may be mordanted with titanium in a variety of ways. The simplest method, though not the most effective, is to run the goods through a solution of titanic sodium sulphate or of the double oxalate, and then through soda. Better results are obtained by a process which is based upon the dissociation of the titanic chloride (or sulphate) in the fibre. To this end the cotton is first dyed manganese bronze, preferably by steeping in tannic acid, and then treating in a solution containing 1 to 2 grms. permanganate of potash and a like amount of magnesium sulphate per litre. The cotton is then transferred to a bath of titanous sulphate, when the manganese bronze is almost instantly discharged and an equivalent amount of titanium is fixed on the fibre. Should the cotton now possess a yellow colour, this will be due to the tannic acid not having been completely oxidised by the permanganate. For very light shades it is not necessary to use tannic acid, the unbleached cotton being treated directly with permanganate, and then with titanous sulphate. Bleaching and mordanting are thus effected simultaneously. In place of using manganese bronze for the precipitation in the fibre of titanic hydrate, iron-buff, dyed in the ordinary way, can be used. It is thus possible to so load the fibre with titanic hydrate that it burns much less readily than ordinary cotton.

According to another process, patented by J. Barnes in 1896, cotton can be mordanted by steeping it in a solution of tanno-oxalate of titanium of 1° to 2° Tw. for some minutes, then wringing and transferring to a hot solution of common salt. Titanium tannate is thus fixed on the fibre. This process is more rapid and economical than first mordanting with tannic acid and then passing through titanic sulphate. In either case, however, titanium tannate is most suitable as a mordant for basic colours. With mordant colours it does not give satisfactory results.

Raw linen treated for a short time in a hot bath of titanous chloride acquires the shade of orange-brown characteristic of "Brown Holland."

Wool.—According to Hummel,* titanium does not possess any general advantages over chromium and aluminium, though, in some particular cases, it gives distinctly superior results.† Dyeing is commenced with the mordant colour and a little acetic acid, the bath is raised to the boil in the course of

* *Journ. Soc. Dyers and Col.*, 1904, p. 65.
† See also J. Barnes, *ibid.*, 1896, p. 174.

half an hour, and, after boiling for half an hour, addition is made of 15 to 20 per cent. of the mordant solution (solution of titanium sodium sulphate containing 4 per cent. TiO_2) and 7½ to 10 per cent. oxalic acid, after which boiling is continued for twenty to thirty minutes.

Silk.—According to G. H. Hurst,* silk can be mordanted by steeping for three to four hours in a 5 per cent. solution of titanium potassium oxalate or titanium sodium sulphate, and then through a 5 per cent. solution of calcium acetate. Or the silk is first steeped for three to four hours in a 5 per cent. solution of titanous chloride, and then in a 5 per cent. solution of sodium phosphate. The tanno-oxalate may also be used for the purpose, the silk acquiring the characteristic yellow colour of this compound. The mode of procedure is similar to the others, the silk being steeped for three to four hours in a 5 per cent. solution of the tanno-oxalate, after which it is washed.

The colours obtained with mordant dyes on material mordanted with titanium are generally intermediate in shade between those obtained with the same dyestuff on chromium and on aluminium mordant. Especially good results are obtained on titanium mordanted cotton with Alizarin orange, Alizarin yellow (M.L.B.), Coeruleïn, &c.; on wool, with these colours, as also with Alizarin cyanine green (Bayer), Anthracene blue (B.A.S.F.), Brilliant Alizarin blue (Bayer), and Gallocyanine. According to Hummel, logwood yields on titanium mordant a black, which is much more dead than that obtained on chromium mordant. On silk, perhaps the most noteworthy result recorded by Hurst is the yellow obtained with weld.

Titanous Salts as Stripping Agents.—In consequence of their powerful reducing action, the titanous salts are capable of destroying many colours on the fibre which do not readily yield to the action of bleaching powder. The colours most readily affected by these are the azo dyes, notably when dyed on cotton, though certain other colours may also be discharged, or, at least, suitably modified by their use.

COPPER (*Cuprum*), Cu = 63·6.

Copper is bivalent. It is a red-coloured metal of 8·94 specific gravity, which melts at a bright red heat and is slightly volatilised by white heat; it is very malleable and ductile and the best conductor of heat and electricity. Copper does not oxidise either in dry or in moist air at the ordinary temperature; but when strongly heated it is first covered with a thin film of oxide, reflecting the colours of the spectrum, and is slowly converted into scales of oxide of copper. Under the influence of the carbonic acid in the atmosphere it is converted into basic carbonate of copper. Steam is not decomposed by red-hot copper. Hydrochloric acid dissolves this metal only when in a very fine state of division, with evolution of hydrogen. Nitric acid, both concentrated and diluted, dissolves copper, even in the cold, but more rapidly when heated, forming nitrate of copper with evolution of nitrous gases. Sulphuric acid does not act on copper at the ordinary temperature; when heated with the strong acid the metal is dissolved and copper sulphate formed, while sulphur dioxide escapes.

Many valuable alloys contain copper as their chief constituent—*e.g.*, brass and all kinds of bronze.

Copper combines in four proportions with oxygen, of which only the two following possess more than a scientific interest:—

Cuprous Oxide, Cu_2O (Red Oxide).
Cupric Oxide, CuO (Black Oxide).

* *Journ. Soc. Dyers and Col.*, 1903, p. 106.

Cuprous Oxide, Cu_2O, is formed by heating a solution of copper tartrate in caustic soda with grape sugar. It is a bright red powder that does not oxidise in the dry state. It is used in glass painting, and imparts to the glass a fine ruby red colour. A yellow *hydroxide* of the composition $4Cu_2O + H_2O = Cu_8O_3(OH)_2$ is obtained by precipitating cuprous chloride with caustic soda. This compound oxidises readily in the air. Cuprous oxide and hydroxide are readily soluble in ammonia; the colourless solution rapidly becomes blue by oxidation when exposed to the air.

Cupric Oxide, CuO (*Black Oxide* or *Monoxide of Copper*).—Cupric oxide is a black amorphous, slightly hygroscopic powder which is insoluble in water, but dissolves readily in acids. Copper oxide dissolves in ammonia with a beautiful intensely blue colour; the ammonio-cupric liquid has the power of dissolving cellulose (cotton and other vegetable fibres); the presence of considerable quantities of mineral salts prevents the cellulose from dissolving in the liquid or precipitates it from the solution. Cupric oxide gives off its oxygen readily in presence of reducing substances, and acts as an oxidising agent.

Cupric Hydroxide, $Cu(OH)_2$, is obtained as a light blue precipitate on addition of caustic alkalies to the solution of a cupric salt. It can be dried over lime without changing; the freshly precipitated moist hydroxide when dried at 100° becomes black and loses water, a hydroxide ($Cu_3O_2(OH)_2$) being formed. Cupric hydroxide does not dissolve in alkalies and has no acid character; it is a moderately strong binacid base.

Cuprous Salts are little known in the pure state, since most acids decompose them, separating the metal in the free state, and forming cupric salts. The salts are colourless, and rapidly absorb oxygen from the air, forming cupric salts.

Cuprous Chloride, Cu_2Cl_2, is obtained as a solid white substance by dissolving a mixture of metallic copper and cupric oxide in hydrochloric acid.

Cuprous Sulphocyanide or **Thiocyanate,** $Cu_2(CNS)_2$, is used by calico-printers under the name *White Paste.* It is obtained by precipitating a solution of blue vitriol, containing ferrous sulphate or sulphurous acid with potassium sulphocyanide. The white precipitate is insoluble in water. It is used in the production of Aniline black.

Cupric Salts.—Most of the normal salts are soluble in water. The soluble salts redden blue litmus, and have a disagreeable taste; they are decomposed at a low red heat, except blue vitriol, which withstands a slightly higher temperature. The salts are white in the anhydrous state; when they contain water they have a blue or green colour, which is perceptible in very diluted solutions. All compounds of copper are poisonous.

Caustic potash and soda precipitate from the solutions cupric hydroxide; alkaline carbonates precipitate insoluble basic cupric carbonate; ammonia in excess produces an intensely blue solution of a basic double salt; the carbonate of ammonia acts in the same manner. Sulphuretted hydrogen and ammonium sulphide precipitate from solutions of copper salts black *copper sulphide* (CuS), which is insoluble in diluted acids and in alkalies and little soluble in alkaline sulphides. Metallic iron in contact with solutions of copper salts is immediately coated with a film of copper, and is rapidly dissolved; the copper in the salt is replaced by iron—$Fe + CuSO_4 = FeSO_4 + Cu$.

Basic Salts of Copper are insoluble in water.

Cupric Sulphate, $CuSO_4 + 5H_2O$—*Blue Vitriol, Blue Stone, Copper Sulphate.*—Cupric sulphate is manufactured by roasting ores which contain copper and by dissolving them in sulphuric acid. From this solution crystals having different degrees of purity are obtained; the chief impurity is iron.

Cupric sulphate crystallises in transparent, blue triclinic crystals, which contain only 5 molecules of water of crystallisation, whereas the other metallic sulphates, known as "vitriols"—*e.g.*, ferrous sulphate—contain 7 molecules. 100 parts of water dissolve at—

10° C.	20° C.	30° C.	50° C.	70° C.	90° C.	100° C.
Parts. 37	Parts. 42	Parts. 49	Parts. 66	Parts. 95	Parts. 156	Parts. 203

Blue vitriol is insoluble in absolute alcohol, and but slightly soluble in diluted alcohol. It loses 4 molecules of water at 100° and the last at 220° to 240°, forming a white mass. The anhydrous salt attracts water readily, and turns blue; use is made of this reaction to demonstrate the presence of water in organic liquids—*e.g.*, alcohol. Blue vitriol is extensively used in the arts; for example, in the manufacture of copper colours, and in dyeing.

Cupric Chloride, $CuCl_2$, is formed when copper is acted upon by chlorine gas, or when cupric oxide or carbonate is dissolved in hydrochloric acid. It forms a brownish-yellow powder in the anhydrous state, and crystallises in bluish-green rhombic crystals ($CuCl_2 + 2H_2O$). Cupric chloride is very soluble in water and in alcohol, and is deliquescent. The alcoholic solution burns with a beautiful green flame, and gives the Bunsen flame a green rim, by which reaction minute quantities of copper may be detected, *e.g.*, on the textile fibres.

Cupric Nitrate, $Cu(NO_3)_2$, is obtained by dissolving copper or cupric oxide in nitric acid. Calico-printers prepare it also by the double decomposition of blue vitriol and lead nitrate. The salt forms fine blue prisms, $Cu(NO_3)_2 + 3H_2O$. On being heated to 65° nitric acid is given off; hence the anhydrous salt is not known. Cupric nitrate is very soluble in water and is deliquescent. Since it is decomposed at comparatively low temperatures it is a strong oxidising agent.

Cupric Carbonate, $CuCO_3$, is not known in the pure state. By adding a solution of an alkaline carbonate to a cupric salt, a basic salt, $CuCO_3 + Cu(OH)_2$, is obtained which is insoluble in water. Various minerals consist of basic cupric carbonates.

Cupric Acetate, $Cu(C_2H_3O_2)_2 + H_2O$, is obtained by dissolving cupric oxide, verdigris, or a carbonate of copper in acetic acid, or by the double decomposition of copper vitriol and lead acetate. It forms dark bluish-green monoclinic crystals, which effloresce in the air and dissolve in 13·4 parts of cold and in 5 parts of hot water, also in alcohol. The solution gives off acetic acid on boiling. An *acid salt*, $Cu(C_2H_3O_2)_2C_2H_4O_2 + H_2O$, has been prepared.

Basic cupric acetate or *blue verdigris* is $2Cu(C_2H_3O_2)(OH) + 5H_2O$. It is prepared by placing sheets of copper into acetic acid or into the fermenting husks of grapes. The salt forms blue crystals, and occurs in commerce in greenish-blue lumps, which also contain basic cupric carbonate and sometimes gypsum. On treatment with water the salt is decomposed into the normal and a more basic salt: *green verdigris*, $2Cu(C_2H_3O_2)_2CuO$. Still more basic cupric acetates are also known.

Copper Sulphide, CuS, is obtained as a black precipitate by passing a current of sulphuretted hydrogen through a solution of a copper salt. Laubei gives the following instructions for preparing copper sulphide: mix 1250 grms. ($1\frac{1}{4}$ lbs.) of flowers of sulphur with 5 litres ($\frac{1}{2}$ gall.) caustic soda (70° Tw.), and heat on the water-bath, with frequent stirrings, until all is dissolved; pour

the solution, with constant stirring, into a solution of 6 kgs. (6 lbs.) of blue vitriol in 150 litres (15 galls.) of tepid water, allow the precipitate to settle, and wash it several times with tepid water, by decanting; to the filtered paste of copper sulphide, which should amount to 12 kgs. (12 lbs.), add 15 grms. (½ oz.) of ammonium sulphide, in ½ litre (1 pint) of water to protect the copper sulphide against the oxidising action of the air and store it in vessels in which it is protected from the air. Copper sulphide is insoluble in water, in diluted acids, and in alkalies; by oxidation it is readily converted into cupric sulphate. It is used in the printing and dyeing of Aniline black.

APPLICATION OF THE SALTS OF COPPER TO THE TEXTILE FIBRES.

The salts of copper are chiefly used in dyeing as oxidising agents. They act as carriers of oxygen, which they readily give up to oxidisable substances, and take up again from the air or from bodies which are easily deoxidised. The fastness to light of a great many colours is very considerably increased by a treatment with soluble copper salts—*e.g.*, logwood and many cotton colours—and for this reason copper sulphate finds an extensive application in cotton- and wool-dyeing. The cause of this fact has been found to be the formation of a lake between the dyestuff and the copper, especially in the case of paranitraniline.*

Application to the Vegetable Fibres.—Copper salts are employed in cotton-dyeing and cotton-printing as oxidising agents, in the way above mentioned, for the production of Cutch browns and Logwood blacks; they serve, however, to a certain extent as actual mordants. Copper sulphate is frequently employed in the black-dyeing of cotton warp in union goods, and is fixed for this purpose by means of tannin. Copper sulphide is used in the production of Aniline black by printing, while copper sulphate is largely used in the dyeing of Aniline blacks on piece goods. Copper sulphate is, as indicated above, frequently used for rendering certain colours—*e.g.*, Benzoazurin, Diamine blues, Sulphide browns—faster to light, by treatment with salts of copper.

Solutions of cupric hydroxide in ammonia dissolve cellulose, and are, therefore, used for waterproofing cotton fabrics, the dissolved cellulose filling the interstices of the meshes of the tissue.

Application to Wool.—Copper sulphate is used in conjunction with aluminium sulphate and with ferrous sulphate in the dyeing of logwood blues and logwood black. It is also frequently employed along with bichromate of potash in the mordanting of wool. Generally the natural mordant-dyestuffs resist the bleaching action of the light best when dyed on copper mordants. Very often copper sulphate is used as a saddening agent after the wool has been boiled in a decoction of the colouring matter..

Application to Silk.—Copper sulphate and acetate are used in saddening certain shades of logwood black on silk.

LEAD (*Plumbum*), Pb = 206·9.

Lead is bivalent or tetravalent. It is a bluish-white, bright and very soft metal of 11·3 specific gravity; it melts at 334° C. and boils at a white heat; it possesses little tenacity and elasticity. The bright surface of the metal

* W. Schaposchnikoff, *Zeitschrift Farben- und Textil-Chemie*, 1904, p. 422; see also Ed. Justin-Mueller, *Bull. Soc. Ind. de Rouen*, 1904, No. 2.

becomes tarnished in moist air by the formation of a film of oxide. Lead when melted in open vessels is oxidised and on the surface forms a mixture of lead and lead oxide, so-called lead ashes. Lead is a very useful metal, which could hardly be replaced in many industries, since it is very slowly acted upon by acids, especially at the ordinary temperatures. Acetic acid makes an exception to this rule, so do hydrochloric and nitric acids.

Lead is a constituent of many important alloys, such as solder, pewter, &c.

Lead forms the following five oxides:—

Lead Suboxide, Pb_2O.
Lead Monoxide or Litharge, PbO.
Lead Sesquioxide, Pb_2O_3.
Red Lead or Red Oxide of Lead, Pb_3O_4.
Lead Dioxide or Peroxide, PbO_2.

The suboxide and sequioxide are of no practical importance.

Lead Monoxide, PbO, is obtained by melting lead with access of air. It forms a straw-coloured powder, called *Massicot;* or, when fused at red heat, lemon-yellow to orange-coloured scaly crystals, called *Litharge.* It has a specific gravity of 9·36, is not soluble in water, but imparts to the latter an alkaline reaction by generating the hydroxide. It dissolves in hot solutions of caustic potash or soda, as also in nitric and acetic acid; in most of the other mineral acids it is insoluble. It has basic properties; for example, it saponifies fats, forming lead salts of the fatty acids (lead plasters).

Lead Hydroxide, $Pb(OH)_2$, is precipitated from the solutions of lead salts by caustic alkalies as a white voluminous mass; it is soluble in an excess of caustic potash or soda, forming *plumbates;* but is not soluble in ammonia. Lead hydroxide has a very feeble acid character; but it is a fairly strong diacid base.

Red Lead, Pb_3O_4, is obtained by heating massicot in the air; it is a heavy fiery-red powder, insoluble in water. It is used as a pigment, in glass making, and as a paint to prevent iron from rusting, and as a packing for water- and steam-joints.

Lead Dioxide or Peroxide, PbO_2, also called *puce-coloured oxide of lead,* is obtained by treating red lead with nitric acid. It forms a brown powder which is insoluble in water. It is not readily attacked by acids, and does not form salts with them. Lead peroxide dissolves in hot solutions of caustic potash or soda forming alkaline *plumbates* (Na_2PbO_3 and K_2PbO_3). Lead peroxide and the plumbates are strong oxidising agents.

Lead Salts are generally colourless; those which are soluble in water redden blue litmus and have a disagreeable sweet metallic taste. All lead salts are very poisonous. Caustic alkalies precipitate from the solutions the hydroxide which redissolves in an excess of caustic potash or soda, but not of ammonia. Soda precipitates basic carbonate of lead. Hydrochloric acid and chlorides form a precipitate of lead chloride, which is soluble in much water. Sulphuric acid and sulphates precipitate insoluble sulphate of lead. Chromates precipitate chromate of lead (Chrome yellow), which is readily soluble in caustic potash or soda.

Sulphuretted hydrogen or sulphide of ammonium forms a precipitate of black lead sulphide, which is insoluble in alkaline sulphides, acids and alkalies; by hot nitric acid it is slowly decomposed. Lead salts, notably *white lead,* blacken in an atmosphere containing even traces of sulphuretted hydrogen, lead sulphide being formed.

Lead Nitrate, $Pb(NO_3)_2$, is prepared by dissolving the requisite amount of litharge in hot dilute nitric acid. A solution of the *basic nitrate of lead,* $Pb(NO_3)(OH)$, is obtained by boiling a solution of the normal salt with the calculated amount of litharge.

Lead nitrate crystallises in regular crystals; it is sold in the form of irregular lumps and frequently contains copper as an impurity. In alcohol it is almost insoluble. 100 parts of water dissolve at—

0° C.	10° C.	25° C.	45° C.	65° C.	85° C.	100° C.
Parts. 39	Parts. 48	Parts. 60	Parts. 80	Parts. 101	Parts. 120	Parts. 139

Lead Acetate, $Pb(C_2H_3O_2)_2 + 3H_2O$—*White Sugar of Lead*—Lead acetate is prepared by dissolving the calculated amount of litharge in hot acetic acid. The pure product, which contains over 99 per cent. of crystallised salt ($Pb(C_2H_3O_2)_2 + 3H_2O$), is called white sugar of lead. With crude acetic acid (pyroligneous acid) *brown sugar of lead* is prepared, which contains less than 90 per cent. of the pure salt. By using an excess of litharge, *basic acetate of lead*, $Pb(C_2H_3O_2)(OH)$, and still more basic salts are obtained.

The normal salt forms monoclinic crystals, which effloresce in the air and melt at 75°.

Lead acetate dissolves in about two parts of water at the ordinary temperature and is readily soluble in diluted, not in absolute, alcohol. The solutions of lead acetates rapidly absorb carbon dioxide from the atmosphere and become turbid by formation of the carbonate.

White lead is a basic carbonate of lead.

APPLICATION OF THE LEAD SALTS TO THE TEXTILE FIBRES.

Acetate and nitrate of lead are frequently used in the preparation of mordants, since they readily exchange their acid for sulphuric acid by double decomposition, sulphate of lead being insoluble. Except for the production of Chrome yellows the lead salts are little used in dyeing. The colours are liable to be blackened by sulphuretted hydrogen and are not brilliant. They are poisonous.

Cotton seems to possess some affinity for lead, since it retains the same with great tenacity. Chrome yellow and Chrome orange are produced extensively on cotton by impregnating the fibre with a lead salt and passing through bichromate. In this case the lead salt may be considered to act as a real mordant. In conjunction with fatty acids lead salts serve also as mordants for the eosins.

Silk is sometimes weighted with basic acetate of lead.

MANGANESE, Mn. = 55.

Manganese is a metal which is either di-, tetra-, hexa-, or hepta-valent, and forms the following six oxides:—

Manganese Monoxide or Manganous Oxide, MnO.
Red Manganese Oxide or Mangano-Manganous Oxide, Mn_3O_4.
Manganese Sesquioxide or Manganic Oxide, Mn_2O_3.
Manganese Dioxide or Black Oxide of Manganese, MnO_2.
Manganic Anhydride (not known in the free state), MnO_3.
Manganese Heptoxide, Mn_2O_7.

Manganese Monoxide, MnO, is a greenish powder which rapidly absorbs oxygen, forming red oxide (Mn_3O_4).

Manganous Hydroxide, $Mn(OH)_2$, is precipitated from the solutions of manganous salts as a white gelatinous mass that rapidily turns brown by absorption of oxygen. It is soluble in most acids and is a binacid base; the salts are colourless or pink and do not absorb oxygen. Manganous hydroxide is insoluble in caustic alkalies. Sulphide of ammonium precipitates manganous sulphide from the solutions of manganous salts; sulphuretted hydrogen has little action except in the presence of free alkali.

Manganic Oxide, Mn_2O_3, is formed as a black powder when one of the other oxides is heated in oxygen gas.

Manganic Hydroxide, $Mn_2(OH)_6$, is a dark brown precipitate obtained by the oxidation of manganous hydroxide. It is a weak hexa-acid base, insoluble in alkalies and not readily soluble in acids. It does not form well-defined salts.

Manganese Dioxide, MnO_2, peroxide of manganese, the common black ore of manganese or pyrolusite, is a dark grey, almost black, crystalline mass.

Manganese dioxide forms hydroxides, which act as very weak bases and acids; the salts which it forms with acids are called manganic salts; those in which it combines with bases are the manganites. Manganese dioxide dissolves in cold hydrochloric acid without evolution of chlorine; but on heating it, the $MnCl_4$ dissociates into manganous chloride and chlorine:—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O;\ MnCl_4 = MnCl_2 + Cl_2.$$

The use of manganese dioxide in the manufacture of chlorine gas, chloride of lime, and chlorates, is based on this reaction.

Manganic Acid, H_2MnO_4, is not known in the free state, neither is the anhydride (MnO_3). *Potassium Manganate*, K_2MnO_4, is obtained as a bright green mass when an oxide of manganese is fused in the air with caustic potash. The aqueous solution yields this salt in a crystalline form; on standing, however, or when acidified, the green colour of the solution is changed into bright purple and a new salt is formed: *Potassium Permanganate*, $KMnO_4$ (see below), whilst hydrated manganese dioxide is deposited:—

$$3K_2MnO_4 + 4HCl = 2KMnO_4 + Mn(OH)_4 + 4KCl.$$

Inversely potassium permanganate is reduced to potassium manganate by boiling it with a concentrated solution of caustic soda and by the limited action of reducing agents.

Manganese Heptoxide, Mn_2O_7, and the hydrate, *Permanganic Acid*, $HMnO_4$, are unstable and little known compounds.

Manganous Chloride, $MnCl_2$, is obtained as a bye-product in the manufacture of chlorine from hydrochloric acid by means of manganese dioxide (see above). It forms monoclinic pink-coloured deliquescent crystals, which contain 4 molecules of water of crystallisation. It is soluble in water and in alcohol; the alcoholic solution when ignited burns with a red flame. 100 parts of water dissolve at 10°, 150 parts; at 31°, 269 parts; and at 62·5°, 625 parts of the salt, $MnCl_2 + 4H_2O$. The strong aqueous solution is known by the trade as bronze liquor.

Manganous chloride is used in dyeing cotton manganese brown or bronze. The cotton is impregnated with a solution of the salt, passed through caustic alkali, and the precipitated hydroxide is oxidised by the air or other oxidising agents to form brown manganic hydroxide. The oxidising power of manganic hydroxide which has been thus deposited in the fibre may be used for the production of Aniline black. The product comes into commerce as a reddish solution at about 70° Tw. It often contains calcium chloride as an impurity.

Potassium Permanganate, $KMnO_4$—*Permanganate of Potash.*—Potassium permanganate is found in commerce in the form of almost black crystals with a steel-blue lustre; it dissolves with an intense crimson colour in 15 to 16 parts of cold water.

Potassium permanganate is a very powerful oxidising agent in acid, in alkaline, and in neutral solutions. Hence it is largely used in the laboratory and as a disinfectant, and it is sometimes employed to destroy colours on the fibres which cannot be removed in any other way. Some dyers use it to produce manganese-bronze, and it has also been suggested as a substitute for chlorine in the "preparing" of wool for printing.

ANTIMONY (*Stibium*), Sb = 120·2.

Antimony is tri- and pentavalent. It resembles phosphorus and arsenic in some respects; but it bears still greater resemblance to the metals. It is considered by some as a metal, by others as a metalloid. Antimony forms a bluish-white crystalline, brittle mass of 6·8 specific gravity. It is a constituent of many important alloys—*e.g.*, type metal, Britannia metal, and anti-friction metal. Compounds of antimony are used in pharmacy and in dyeing.

Antimony forms the following compounds with oxygen:—

Antimony Trioxide, Sb_2O_3; Antimonious Acid, $HSbO_2$.
Antimony Tetroxide, Sb_2O_4; Hypoantimonious Acid, $H_2Sb_2O_5$.
Antimony Pentoxide, Sb_2O_5; $\begin{cases}\text{Antimonic Acid, } HSbO_3. \\ \text{Metantimonic Acid, } H_4Sb_2O_7.\end{cases}$

Antimony Trioxide, Sb_2O_3, is found in nature, and can be prepared by heating antimony in the air or with diluted nitric acid; It forms white crystals, which melt at a red heat; it is very sparingly soluble in water, not soluble in nitric acid, but dissolves in hydrochloric, sulphuric, or tartaric acid, and in caustic alkalies.

Antimony trioxide forms a hydroxide, *antimonious acid*, $HSbO_2$. This compound acts both as an acid and a base. The acid character does not offer any practical interest. As a base it is monovalent and trivalent; in the monovalent state it is considered to be combined with oxygen, forming the monovalent radical *antimonyl*, SbO. The salts which antimony forms with acids, when soluble in water, redden blue litmus, and possess a very disagreeable metallic taste. They are dissociated by water, antimony trioxide being thrown down, and an acid salt remaining in solution. Caustic alkalies and the alkaline carbonates precipitate from the solutions of antimony salts antimonious hydroxide ($HSbO_2$), which is converted into antimony trioxide on boiling. The hydroxide is soluble in an excess of caustic potash and soda. Sulphuretted hydrogen precipitates from acidified solutions of the salts orange-red antimonious sulphide (Sb_2S_3), which is soluble in alkaline sulphides.

Antimony and its compounds are poisonous. Since it shows reactions similar to arsenic, it is sometimes mistaken for the latter; the poisonous effects of antimony and arsenic, however, are totally different.

The application of compounds of antimony in dyeing is limited to the salts of antimony trioxide, and these are employed exclusively in dyeing and printing of cotton and linen. Their usefulness is based on the fact that tannic acid forms a lake with antimony trioxide, which is insoluble in tannic acid. Faster colours are obtained with antimony tannate than with tannic acid alone (see p. 189).

Antimonious Sulphate, $Sb_2(SO_4)_3$, separates from the solutions of antimony trioxide in hot conc. sulphuric acid on cooling. It is dissociated by water into an insoluble basic and a soluble acid salt.

Antimonyl Sulphate, $(SbO)_2SO_4$, is obtained by dissolving antimony trioxide in moderately diluted sulphuric acid. It is dissociated by water, like the preceding compound.

Antimony Chloride or Trichloride, $SbCl_3$, is formed by the action of chlorine on antimony. It is prepared by dissolving antimony trioxide or sulphide in hydrochloric acid, and can be evaporated to dryness from this solution. It forms a soft, crystalline, colourless mass, which melts at 73°, and volatilises at 223°; it is deliquescent, and is dissociated by much water, according to the equation—$SbCl_3 + H_2O = SbOCl + 2HCl$.

Antimony Fluoride, $SbFl_3$, is obtained by dissolving antimony trioxide in hydrofluoric acid. The salt forms colourless rhombic pyramids, which are deliquescent; by dilution with water it is not decomposed; on evaporating the solution without excess of hydrofluoric acid a basic fluoride is obtained. Antimony fluoride attacks glass and metals, except lead and platinum. It is kept in wooden casks.

Antimony fluoride forms crystalline double salts with one, two, or three equivalents of the fluorides, chlorides, and sulphates of the alkalies.

Antimony Sodium Fluoride, SbF_3NaF, has been brought into the market by R. Koepp & Co., in Oestrich a. Rh. (Germany), under the name of *double antimony fluoride*. It crystallises in triclinic prisms, and is readily soluble in water; 100 parts of cold water dissolve 63 parts of the salt, and 100 parts of hot water 166 parts. The solution can be diluted without dissociation. It reacts slightly acid, and corrodes glass and metals.

The salt contains 66 per cent. Sb_2O_3 (*i.e.*, the corresponding amount of SbF_3), and 658 grms. are equivalent to 1,000 grms. of tartar emetic.

A double salt of antimony fluoride and ammonium sulphate, $SbF_3(NH_4)_2SO_4$, has been patented, and is sold by E. de Haën, List vor Hannover (Germany), under the name of *antimony salt*. It forms white oblique crystals, and dissolves very easily in water—140 parts of the salt in 100 parts of water; the solution possesses a strongly acid reaction, and attacks glass and metals like the other fluorides. It is not dissociated by dilution. The salt contains an amount of antimony fluoride corresponding to 47 per cent. Sb_2O_3—*i.e.*, 9 parts of antimony salts are nearly equivalent to 10 parts of tartar emetic. A number of similar salts are sold by various firms as substitutes for tartar emetic.

Double Oxalate of Antimony and Potassium, $SbK_3(C_2O_4)_3 + 4H_2O$, has been introduced to the dyeing trade by R. Koepp & Co. in Oestrich. The salt is obtained by dissolving antimony trioxide in acid oxalate of potash, and crystallises in fine needles, which are stable in the air, and dissolve most readily in either cold or hot water. The solution of the salt dissociates rapidly, forming an insoluble basic oxalate of antimony and soluble acid oxalates. The double oxalate contains only 25·1 per cent. Sb_2O_3; it has been stated, however, that it can replace equal quantities of tartar emetic, although the latter contains 43·4 per cent. Sb_2O_3. Noelting has explained this surprising fact by experiments, showing that acid potassium oxalate does not prevent the formation of antimony tannate to the same extent as acid potassium tartrate, which is generated from tartar emetic. On the other hand, the double oxalate dissociates more rapidly than the double tartrate, thus yielding its antimony more readily, and for these two reasons it is more effective.

Double Tartrate of Antimony and Potassium or Tartar Emetic, $(SbO)KC_4H_4O_6 + \frac{1}{2}H_2O$, was introduced into the dyeing trade by Thomas Brooke of Manchester, who was the first to use an antimony salt for the fixation of basic colours by means of tannic acid, and was rewarded for his invention by the Société Industrielle de Mulhouse with a gold medal.

Tartar emetic is obtained by boiling antimony oxide with a solution of

tartar, and crystallises with half a molecule of water in rhombic octahedra which lose water by efflorescence. The salt is not very soluble in water, and insoluble in alcohol. One part of tartar emetic, $(SbO)KC_4H_4O_6 + \frac{1}{2}H_2O$, requires for its solution at—

8·7 C.	21° C.	31° C.	50° C.	75° C.
Parts Water. 19	Parts Water. 12·6	Parts Water. 8·2	Parts Water. 5·5	Parts Water. 3·2

The solution dissociates into insoluble basic antimony tartrate and soluble acid tartrates. Pure antimony-potassium tartrate, $(SbO)KC_4H_4O_6 + \frac{1}{2}H_2O$, contains 43·4 per cent. Sb_2O_3.

The commercial product is sold at a strength of 43 per cent. Sb_2O_3 in fine crystals or irregular lumps. The article is subject, however, to adulteration either with cheaper antimony salts or with other substances; it may contain the required quantity of antimony without being genuine tartar emetic.

Antimony Lactate has been patented* for the same applications in dyeing and printing for which the other antimony salts are used. The salt is said to be not crystallisable, very soluble in water, and not to dissociate. It does not appear to be offered to the trade.

Double Bilactate of Antimony and Calcium or Antimonine, $[(SbO)(C_3H_5O_3)]_2Ca_3(C_3H_5O_3)_4 2C_3H_6O_3$, is obtained by treating antimony oxide with calcium bilactate. The dry salt forms a white crystalline and very hygroscopic mass containing 27 per cent. Sb_2O_3, whilst the commercial product "*Antimonine,*" which is manufactured by C. H. Boehringer Sohn in Ingelheim on the Rhine, contains 15 per cent. Sb_2O_3.

APPLICATION OF THE COMPOUNDS OF ANTIMONY TO THE TEXTILE FIBRES.

Tannic acid is employed in the dyeing of cotton and linen as a mordant, because it forms lakes with the basic dyestuffs, which are insoluble in water. An excess of tannic acid, the presence of which is unavoidable, dissolves these lakes, hence the colours thus obtained do not resist washing and soaping, and are liable to bleed. It has been found, however, that tannic acid can be transformed by certain metals, for example, by tin, aluminium, iron, and zinc, but best of all by antimony, into insoluble salts, which have the same power as is possessed by the free acid to precipitate basic dyestuffs in the fibres, but have no dissolving action on the colour lakes. These double lakes have the additional advantage of resisting the bleaching action of light better than the simple tannates.

Thomas Brooke, as has been mentioned, discovered the use of antimony salts in the form of tartar emetic for the fixation of Aniline colours. Tartar emetic, however, is a very expensive article, since the tartaric acid in it has a much higher value than the antimony. A number of substitutes, notably the double oxalate and various fluorides, have, therefore, been introduced, which are sold at considerably lower prices and give more or less satisfactory results. Tartar emetic has been very generally replaced by other salts of antimony.

The application of the antimony salts is very simple. The goods which have been mordanted with tannic acid are slightly rinsed in cold water to

* Ch. N. Waite, U. S. Patent 341,294.

remove loosely adhering mordant and then worked for one-quartei of an hour in the tepid solution (30° to 60°) of the antimony salt. The bath can be used continuously, if the liberated acid is neutralised from time to time. The goods which have been worked in the antimony bath are wrung out and must be well washed in water before dyeing; a hot soaping improves the ultimate shade as to brilliancy and is advisable for some colours—*e.g.*, Methylene blue. The washing must be done with the greatest care, since loosely adhering antimony tannate, unless removed before dyeing, will be the cause of rubbing and smearing of the colour. Moreover, antimony is a strong poison, and such loosely adherent particles are liable to cause serious affections of the skin. It must be stated, however, that accidents of poisoning do not appear to have been observed in connection with antimony mordants, not even in the knitting mills of Nottingham or Chemnitz, where yarns mordanted with antimony are worked up in great quantities.

In printing, the application is different in so far as the goods are printed on with a mixture of tannic acid and dyestuff, steamed, and subsequently passed through the antimony bath. In printing, the lake formed by tannic acid and dyestuff is transformed into the triple antimony lake; whereas in dyeing antimony tannate is formed first and combines subsequently with the dyestuff.

In the dyeing of cotton and linen goods a solution of 5 to 10 parts of tartar emetic in 1,000 parts of water is used; the tannic acid previously absorbed by the fibre extracts antimony from this solution, whilst an acid potassium tartrate is left behind, which impedes and prevents the formation of antimony tannate. This acid salt can be neutralised by the addition of sodium carbonate; but it is difficult to regulate properly the quantity of soda to be added; better results are obtained by adding to the solution a small quantity of ground chalk which dissolves more gradually.

Antimony potassium oxalate is used of the same strength as tartar emetic, although it contains only about half as much antimony; it is best to use 5 to 10 parts per 1,000 parts of water; greater quantities give less satisfactory results. The action of the oxalate is more rapid than that of the tartrate; it works best in diluted baths and by short immersion. Calcareous water should be avoided, since it precipitates oxalic acid; and the addition of soda does not appear to be advantageous.

The fluorides, as a rule, are very acid and must be neutralised with soda; about one-fifth to one-fourth of their weight of soda crystals is required. The usual strength employed is 5 to 20 parts of salt to 1,000 parts of water; it yields good results, but the shades are not exactly the same as those obtained with tartar emetic.

Antimonine is used in the same quantities as tartar emetic, with the addition, however, of 2 parts of acetic acid for 1,000 parts of liquor, the lactate being very easily dissociated and yielding its antimony even in the acid liquor very readily.

In *silk dyeing*, antimony salts are also used in connection with tannins to render basic or acid colours faster to water and washing (see p. 191).

ZINC, Zn = 65·4.

Zinc is bivalent. It is a bluish-white metal of 6·9 specific gravity, exhibits crystalline structure, and is brittle at the ordinary temperature, but it can be rolled out at 130° C. It melts at 423°, and volatilises at a bright red heat; it takes fire at this temperature and burns with a luminous green flame, forming zinc oxide (ZnO). Zinc is not acted upon by dry or moist air, nor is it affected by water; but it dissolves readily

in dilute acids or in solutions of caustic potash or soda, with the evolution of hydrogen.

Zinc is much used in the metallic state in the form of sheets, and is employed as a coating for iron to protect the latter metal from rust; the iron which has thus been coated is, incorrectly, called galvanised iron. Zinc dust, which is formed in great quantities by the metallurgical distillation of zinc, consists of a mixture of finely-divided zinc and zinc oxide; it is an excellent reducing agent in acid, and especially in alkaline solutions. It is used both in the laboratory and in the arts; for instance, for the preparation of indigo-vats.

Zinc forms a number of industrially important alloys.

Zinc Oxide, ZnO, is a white substance which is obtained by the oxidation of zinc or by igniting the carbonate or nitrate. Zinc oxide forms the white pigment called *zinc white*, which has the advantage of not being discoloured by sulphuretted hydrogen. It is used in printing (especially on linings) as a body colour, and also to increase the action of formaldehyde-sulphoxylate discharges.

Zinc Hydroxide, $Zn(OH)_2$, is precipitated as a white amorphous mass from the solutions of zinc salts by caustic potash, soda, or ammonia; by an excess of either precipitant it is readily redissolved. Neither zinc oxide nor zinc hydroxide are soluble in water, but freely soluble in caustic alkalies and dilute acids. Zinc hydroxide is a diacid base and a weak di-basic acid. The compounds with bases are called *zincates;* they are formed by dissolving zinc or zinc oxide or zinc hydroxide in caustic alkalies; for instance, according to the equations—

$$Zn + 2NaOH = Zn(ONa)_2 + H_2 \text{ or } Zn(OH)_2 + 2NaOH = Zn(ONa)_2 + 2H_2O.$$

The zincates of the alkalies are precipitated by the salts of the other metals, forming zincates with the latter, for instance—

$$Zn(ONa)_2 + MgCl_2 = ZnO_2Mg + 2NaCl \text{ or } 3Zn(ONa)_2 + Al_2(SO_4)_3 = (ZnO_2)_3Al_2 + 3Na_2SO_4.$$

By means of this reaction, compound mordants, consisting of two or three different metals, are precipitated in the fibre. The goods are first impregnated with acetate of aluminium or chromium, for instance, and subsequently passed through sodium zincate; a triple mordant, consisting of aluminium, magnesium, and zinc, is obtained by passing the material, first, through a mixture of the acetates of aluminium and magnesium, and, subsequently, through sodium zincate. An extensive study of the compound mordants has been published by Prudhomme * in the *Bulletin de Mulhouse*, 1891.

The *zinc salts* are colourless and soluble in water or in acids. The neutral salts, which are soluble in water, redden litmus, possess a disagreeable metallic and astringent taste, and are poisonous.

Zinc Sulphate or *White Vitriol*, $ZnSO_4 + 7H_2O$, crystallises in long prisms, and is isomorphous with Epsom salt (magnesium sulphate). It is efflorescent in the air and loses six molecules water at 100°; it is decomposed by white heat.

The anhydrous salt, $ZnSO_4$, dissolves in twice its weight of cold water, and 100 parts of cold water dissolve about 135 parts, and 100 parts of hot water 655 parts of the crystallised salt. Zinc sulphate is used for weighting cotton goods, and sometimes in dyeing wool with the basic colours.

Zinc Chloride, $ZnCl_2$, is a white, soluble, deliquescent substance. The aqueous solution gives off hydrochloric acid on boiling, and a basic salt, *zinc oxychloride*, ZnCl(OH), is formed, which can also be obtained by boiling zinc chloride with oxide or hydroxide of zinc. By adding water to the solution of the basic salts, precipitates of varying composition are obtained, consisting of

* *Journ. Soc. Dyers and Col.*, 1891, p. 133.

the zinc oxychloride and of zinc hydroxide. By boiling a solution of zinc chloride (1·70 sp. gr.) with an excess of zinc oxide a solution is obtained, which dissolves silk. This solution is used in the analysis of mixed fabrics to separate silk from wool and from the vegetable fibres.

Zinc chloride is a strong dehydrating agent, and is frequently employed as such in the laboratory. It is largely used as a constituent of the size for cotton goods. Its action is simultaneously hygroscopic and antiseptic.

Zinc Nitrate, $Zn(NO_3)_2 + 6H_2O$, is a crystalline deliquescent salt. On being heated to 100° it loses water and nitric acid, and a basic salt is formed.

Zinc nitrate is used by printers, and is prepared either by dissolving zinc in nitric acid or by the double decomposition of zinc sulphate and lead nitrate; iron can be removed from the solution of this salt by boiling it with zinc oxide. Zinc nitrate is added to the thickened mordants, since it prevents the thickening from prematurely decomposing. On account of its hygroscopicity it is also sometimes added to colours in woollen printing.

Zinc Carbonate, $ZnCO_3$, occurs native as calamine. It is obtained by precipitating a zinc salt with acid potassium carbonate; if the solution of normal potassium carbonate is added, basic carbonates of zinc of varying composition are thrown down.

Zinc Acetate, $Zn(C_2H_3O_2)_2 + 3H_2O$, forms crystals which are readily soluble in water. This salt has been recommended by Henri Schmid for the fixation of tannic acid instead of tartar emetic; 8 to 10 parts of zinc sulphate and 4 to 5 parts of sodium acetate are added to 1,000 parts of water (see *Basic Colours*).

Zinc Lactate, $ZnC_3H_5O_3$, has been patented by C. H. Boehringer Sohn for mordanting cotton without previous tanning, basic colours and some other of the triphenylmethane series being fixed tolerably well by zinc oxide.

Zinc Ferrocyanide, obtained by double decomposition from zinc sulphate and potassium ferrocyanide, is a good mordant for basic colours, and is produced as such on cotton tissues for illuminating Aniline black.

Nickel, Ni = 58·7.—Nickel is a bi- and tetravalent metal, which resembles iron chemically. It is a white, malleable and tenacious, very hard and magnetic metal of the specific gravity 8·9. It is used in the free state for nickel-plating iron and other metals to protect them from oxygen and acids; it is also a constituent of various alloys, such as German silver, and certain coins.

Nickel forms two oxides, the *monoxide* (NiO) and the *sesquioxide* (Ni_2O_3); the former of these gives rise to nickel hydroxide and to the ordinary nickel salts.

Nickel Hydroxide, $Ni(OH)_2$, is obtained as an apple-green precipitate on addition of caustic potash or soda to the solution of a nickel salt; an excess of the precipitant does not redissolve the hydroxide. It is slightly soluble in water, and dissolves in ammonia with a blue colour. It is stable in the air, and dissolves readily in sulphuric, nitric, or hydrochloric acid to form nickel salts.

Nickel Sesquioxide, Ni_2O_3, is a black powder which dissolves in hydrochloric acid with the evolution of chlorine and formation of the same chloride as is obtained from the preceding nickel oxide.

The *nickel salts* are derived from nickel monoxide, and are prepared by the action of acids on the oxides or on the carbonate. They possess a peculiar apple-green colour; many of them are soluble in water. The most important soluble nickel salts are *nickel sulphate*, $NiSO_4 + 7H_2O$, *nickel chloride*, $NiCl_2$, *nickel-ammonium chloride*, $NiCl_2 . NH_4Cl$, *nickel nitrate*, $Ni(NO_3)_2$, *nickel acetate*, $Ni(C_2H_3O_2)_2$, *nickel nitrate-acetate*, $NiNO_3(C_2H_3O_2)$, and *nickel sulphocyanide*, $Ni(CNS)_2$.

Liechti and Ulrich * have studied the mordanting properties of various nickel salts on cotton. They succeeded in fixing them either by first impregnating the material with a nickel salt and subsequently passing it through soda, or by first mordanting with Turkey-red oil and subsequently with a nickel salt. Many of the nickel salts crystallise in the fibre, and lose their acid very slowly; hence they are little suitable for mordanting. The best results were obtained with the chloride, the nickel-ammonium chloride, the nitrate, the nitrate-acetate, and sulphocyanide; while the sulphate and acetate are less serviceable owing to their great tendency to crystallise. These authors recommend the nickel-ammonium chloride for dyeing, and the nickel nitrate-acetate for printing to produce pure colours in light shades.

The only use made of the nickel salts in dyeing or printing is for the fixation of the nitroso-colours, such as dinitrosoresorcin, &c.

The use of nickel- and cobalt-salts for rendering certain salt colours faster to light has been patented by Aykroyd and Krais, the effect of these salts being similar to that of blue vitriol, but much weaker; they offer, however, the advantage that the shade of some colours is less altered than in the case of copper salts.

W. M. Gardner † has studied the behaviour of nickel sulphate and cobalt sulphate as wool mordants. He found that these salts are fixed best without any oxalic acid, tartar, or other acid being added to the mordanting bath. The salts apparently do not offer advantages over the iron salts, which they resemble in their tinctorial character.

Cobalt, Co = 59.—Cobalt and its compounds resemble nickel and its salts except in colour. The cobalt compounds are distinguished for the brilliancy of their colour; some are employed as pigments, and they impart a magnificent blue tint to glass. There are three oxides of cobalt. The monoxide (CoO) forms with acids the stable *cobaltous salts,* which are pink coloured, such as the sulphate ($CoSO_4 + 7H_2O$) or chloride ($CoCl_2$). The tinctorial properties of the cobalt compounds have been little studied (see *Nickel*).

Vanadium, V = 51·2, is tri- and pentavalent. It forms five oxides, of which the highest, *vanadium pentoxide* (V_2O_5), is the most important. When dissolved in ammonia it yields *ammonium vanadate* (NH_4VO_3) as colourless, transparent, crystalline crusts, soluble in 100 parts of water, but almost insoluble in ammonium chloride solution. The commercial ammonium vanadate is a dirty white powder, and yields, on treatment with hydrochloric acid, a reddish-yellow solution of *vanadyl chloride* ($VOCl_3$), which gives off chlorine; at the same time the solution becomes a fine blue, and contains a vanadium chloride, possibly V_2Cl_4. For practical purposes this blue solution is used and prepared in the following way:—

20 grms. (4 ozs.) of ammonium vanadate in powder are mixed with
100 grms. (20 ozs.) of hydrochloric acid (34° Tw.), and
100 grms. (20 ozs.) of water.
The mixture is heated and
300 c.c. ($\frac{6}{10}$ pint) sodium bisulphite (55 Tw.)

are added in small portions. The reduction takes place immediately.

Vanadium is an exceedingly active carrier of oxygen, and is used, along with chlorate of potash or soda, in printing and dyeing Aniline black. Extraordinarily small quantities of vanadium are sufficient. According to Witz, this substance is still effective in a solution of 1 in 270,000; in practice 0·0012 grm. is used per litre of colour, containing 80 grms. Aniline hydrochloride or $\frac{1}{67000}$ of the weight of this salt.

* *Journ. Soc. Dyers and Col.*, 1887, pp. 81, 93.
† *Ibid.*, 1890, p. 39.

Cerium, Ce = 140·25, has been used for the same purpose as vanadium or copper—*i.e.*, as a carrier of oxygen for Aniline-black and Diphenyl-black printing.

Cerium Bisulphate, $Ce(SO_4)_2 + 3H_2O$, in the pure state is a pink-coloured crystalline powder.

Tungsten or Wolfram, W = 184, is chemically related to chromium. It forms a trioxide, *tungsten trioxide*, WO_3, which is soluble in caustic alkalies. The alkaline solution yields, on addition of acids, a white precipitate of *tungstic acid*, $H_2WO_4 + H_2O$. The alkaline *tungstates* are soluble in water, and are crystalline. *Sodium tungstate*, $Na_2WO_4 + 2H_2O$, crystallises in rhombic tables, and is soluble in 4 parts of cold and in 2 parts of hot water; it evinces an alkaline reaction and a bitter salt-like and astringent taste. A great number of sodium polytungstates are known. By melting wolframite, tungsten ore, with soda ash a sodium tungstate (*sodium paratungstate*, $Na_{10}W_{12}O_{41}$) is obtained. It crystallises at the ordinary temperature in large triclinic crystals which contain 28 molecules of water, but, at elevated temperatures, with less water. It has been unsuccessfully recommended as a substitute for stannate of soda, and is sometimes added to this article to increase the effect of the stannate. Of greater importance is the application of this tungstate for the purpose of rendering textile goods uninflammable; it is especially suitable for this purpose, since it does not affect the fibre nor the colours.

Chromium Tungstate, $Cr_2(WO_4)_3$, is produced by the double decomposition of an alkaline tungstate with chrome alum or chromium chloride, and is sold as a green paste, containing about 40 per cent. of dry matter. It serves as an oxidising agent in Aniline-black printing.

Both tungsten and molybdenum may act as wool mordants, the latter yielding results similar to those obtained with chrome.*

Uranium, U = 238·5, also belongs to the chromium group.

Uranium Sulphate, $U(SO_4)_2 + 8H_2O$, which crystallises in greenish rhombic crystals, has been recommended as a wool mordant,† as it yields fine grey shades with the Alizarins. Uranium salts are poisonous.

VARIOUS CHEMICALS.

Hydrogen Peroxide, $H_2O_2 = \begin{matrix} O-H \\ | \\ O-H \end{matrix}$ —*Oxygenated Water.*—Hydrogen peroxide occurs in small quantities in the air and in rain water, where it is probably produced by the action of ozone on water. It is prepared artificially by dissolving barium peroxide in acidulated water at a moderate temperature. Other peroxides—*e.g.*, those of sodium or calcium—act in the same way. The reaction proceeds according to the equation $BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4$. The barium peroxide must be used as pure as possible, and in a very finely-divided state. Purity is necessary for a high percentage yield, as the slightest impurity causes the yield to be much lessened. The barium peroxide is soaked repeatedly in water to remove any caustic barium oxide, and finally passed through a fine sieve, collected on filters, and made into a paste. For the preparation of hydrogen peroxide the paste is very slowly introduced into dilute sulphuric acid, containing a small proportion of hydrochloric and phosphoric acids; care must be taken that the temperature does not exceed 20° C., and the liquid must be stirred continually in order that the peroxide may never remain in contact with neutral parts of the solution; otherwise

* E. Knecht, *Journ. Soc. Dyers and Col.*, 1897, p. 135.
† W. M. Gardner, *Journ. Soc. Dyers and Col.*, 1890, p. 39.

decomposition takes place immediately, and the yield suffers in consequence.* When the solution is nearly neutralised it is advantageous to add sufficient phosphate of soda to replace the free sulphuric acid by phosphoric acid in the free state, since this substance has a preserving influence on the product. The liquid portion is separated from the sediment, the latter washed with water, and the wash waters are run together and made into a 3 per cent. solution, from which the dissolved baryta can be best precipitated by sodium sulphate.

Hydrogen peroxide in the pure state is a colourless, syrupy liquid of 1·499 specific gravity, which boils under an atmospheric pressure of 26 mm. at 69·2° C. The specific gravity is considerably lowered by small additions of water. The concentrated liquid reacts acid towards litmus; diluted solutions, however, show a neutral reaction. It possesses a bitter, astringent taste, and mixes with water in all proportions. Very diluted aqueous solutions can be boiled without the peroxide being decomposed, a part of it escaping together with the steam.

Recent investigations have shown that pure hydrogen peroxide is fairly stable, and its readiness to decomposition is caused by certain impurities, especially by traces of alkaline compounds and compounds of the heavy metals.

Technically-prepared peroxide is very unstable in concentrated solutions and decomposes readily with evolution of oxygen; in diluted and slightly acidulated (H_3PO_4) solutions it keeps better. The decomposition takes place even at a medium temperature, and, by heating, it can be increased to an explosion. For preserving the strength of the peroxide the addition of 1 grm. naphthalene per litre of peroxide has been recommended by S. Zinno, and by M. Sunder the addition of 2 per cent. of alcohol or ether. In consequence of its easy decomposition, and owing to the fact that oxygen is given off in the nascent state, hydrogen peroxide acts as a powerful oxidising agent. Thus chromium oxide and arsenic (the element) are converted into chromic and arsenic acids respectively, sulphides are transformed into sulphates (*e.g.*, PbS into $PbSO_4$); organic colouring matters are decolourised and destroyed; from sulphuretted hydrogen sulphur, from hydrochloric and hydriodic acids chlorine and iodine respectively are separated—for example, $H_2O_2 + 2HI = I_2 + 2H_2O$.

Hydrogen peroxide acts but slowly on a solution of pure potassium iodide; but iodine is separated immediately on addition of ferrous sulphate (and can be recognised by the reaction on starch paste). The oxides of barium, magnesium, and zinc are oxidised by peroxide of hydrogen into the peroxides; for instance, $MgO + H_2O_2 = MgO_2 + H_2O$. H. Koechlin makes use of this fact in the bleaching of cotton.† (See p. 122.)

In the above cases hydrogen peroxide is an oxidising agent, but some substances are reduced by it, such as unstable oxides like the mercury, silver, and gold oxides; and certain acids such as chromic and permanganic acids.

The quantitative determination of hydrogen peroxide is based on its reaction with potassium permanganate in the presence of acids—

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2.$$

Chlorine in aqueous solution is oxidised to hypochlorous acid and subsequently reduced to hydrochloric acid—

$$1.\ Cl_2 + H_2O_2 = 2HOCl. \qquad 2.\ HOCl + H_2O_2 = HCl + H_2O + O_2.$$

Hydrogen peroxide is also resolved into water and oxygen by many substances in a finely-divided state—*e.g.*, gold, platinum, silver, carbon, or manganese peroxide.

* See also R. Wolffenstein, *Journ. Soc. Dyers and Col.*, 1907, p. 260.
† Prudhomme, *Journ. Soc. Dyers and Col.*, 1891, p. 136.

Commercial peroxide of hydrogen forms a colourless liquid which contains about 3 per cent. H_2O_2 in aqueous solution. The strength of the commercial article is expressed in volumes of available oxygen.

Hydrogen peroxide may be stored in well-tarred casks, in *bright* tin vessels, or in such which have been coated with amber varnish or paraffin wax, or in glass vessels. Since many metals have a catalytic action on the substance, decomposing it into water and oxygen, it is generally used in earthenware or wooden vessels. It should not be exposed to light or heat, and should not be stored in tightly closed vessels, else these might be broken by inside pressure from evolved oxygen.

Hydrogen peroxide is the best bleaching agent known for all classes of fibres. Owing to its high price its application was restricted until recently to the bleaching of tussur silk and feathers; but it is now used in increasing quantities for the bleaching of woollen goods. The practical application has been described under *Bleaching*.

Carbon Bisulphide, CS_2, is produced by passing vapours of sulphur over red-hot charcoal. It is a colourless liquid, usually possessing a peculiar, very disagreeable smell, is very volatile, and boils at 47° C. It has a specific gravity of 1·297 at 0° and is almost insoluble in water, but is miscible with alcohol and ether. It is very inflammable.

Carbon bisulphide is an excellent solvent for sulphur, phosphorus, fatty oils, resins, gums, and india rubber.

Tetrachloride of Carbon or Carbon Tetrachloride is obtained by the action of chlorine or chloride of sulphur on carbon bisulphide. It is a colourless liquid of 1·632 specific gravity, boiling at 76·7° C., insoluble in water, but readily miscible with alcohol, ether, oils, petroleum benzine, and soap. It is not inflammable, and is used in place of petroleum benzine for dissolving india rubber and removing stains from textile fabrics.

Petroleum Spirit, Petroleum Benzine, and Ligroïn are the light oils of American petroleum, and consist chiefly of the saturated hydrocarbons of the fatty series, which correspond to the general formula C_nH_{2n+2}. They possess a specific gravity of 0·65 to 0·73, and boil from 50° to 120°; the lightest of these oils are called petroleum-spirit, the heaviest ligroïn. They are very good solvents for fats, &c., and are largely used for dry cleaning.

Benzene, C_6H_6, is one of the products of the destructive distillation of coal, and occurs in coal tar. It is a colourless, mobile liquid, possessing an ethereal smell, and having a specific gravity of 0·8799 at 20° C.; it solidifies at about 0°, melts at 8°, and boils at 80·5°. It is very inflammable, and burns with a smoky flame. It is not miscible with water, but mixes in all proportions with alcohol and ether. It dissolves very freely sulphur, phosphorus, fats, and resins. Benzene is the raw material for the manufacture of nitrobenzene and aniline, &c., and is also frequently used for dry cleaning, especially in France.

Methyl Alcohol or Wood Spirit, $CH_3(OH)$, is produced by the destructive distillation of wood. It is a colourless, mobile liquid, possessing a pure spirituous smell; the specific gravity is 0·796 at 20° C. and the boiling point 66°. It burns with a non-luminous flame, and is miscible with water, alcohol, and ether. Mixtures of methyl alcohol and water possess nearly the same specific gravity as those of ordinary alcohol and water.

Methyl alcohol strongly resembles ethyl alcohol.

Ethyl Alcohol or Ordinary Alcohol (*Spirits of Wine*), $C_2H_5(OH)$, is the product of the vinous fermentation of sugar—$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$. Pure alcohol, free from water, is called *absolute alcohol*; it is a colourless, mobile liquid, possessing a pleasant spirituous smell and a burning taste. Its specific gravity is 0·789 at 20° C.; and it boils at 78·3°. Alcohol absorbs water from the air with avidity; and mixes with water in all proportions,

heat being evolved, and contraction taking place. It cannot be completely separated from water by distillation; to withdraw all the water the liquid must be distilled with a substance capable of combining with water, such as quicklime or potassium carbonate.

Alcohol is very inflammable, burning with a slightly luminous blue flame. It dissolves many mineral salts, the caustic alkalies, the carbo-hydrates, resins, fatty acids, and a great many other carbon compounds. Most gases dissolve more freely in alcohol than in water. Some salts, such as calcium chloride or magnesium nitrate, form crystalline compounds with alcohol, which plays the part of water of crystallisation.

SPECIFIC GRAVITY OF ETHYL-ALCOHOL AND PERCENTAGE BY WEIGHT AT 60° F. ($15\frac{5}{9}$° C.)—(*Fownes*).

Specific Gravity.	Per Cent. by Weight C_2H_6O.	Specific Gravity.	Per Cent. by Weight C_2H_6O.	Specific Gravity.	Per Cent. by Weight C_2H_6O.
0·9991	0·5	0·9511	34	0·8769	68
0·9981	1	0·9490	35	0·8745	69
0·9965	2	0·9470	36	0·8721	70
0·9947	3	0·9452	37	0·8696	71
0·9930	4	0·9434	38	0·8672	72
0·9914	5	0·9416	39	0·8649	73
0·9898	6	0·9396	40	0·8625	74
0·9884	7	0·9376	41	0·8603	75
0·9869	8	0·9356	42	0·8581	76
0·9855	9	0·9335	43	0·8557	77
0·9841	10	0·9314	44	0·8533	78
0·9828	11	0·9292	45	0·8508	79
9·9815	12	0·9270	46	0·8483	80
0·9802	13	0·9249	47	0·8459	81
0·9789	14	0·9228	48	0·8434	82
0·9778	15	0·9206	49	0·8408	83
0·9766	16	0·9184	50	0·8382	84
0·9753	17	0·9160	51	0·8357	85
0·9741	18	0·9135	52	0·8331	86
0·9728	19	0·9113	53	0·8305	87
0·9716	20	0·9090	54	0·8279	88
0·9704	21	0·9069	55	0·8254	89
0·9691	22	0·9047	56	0·8228	90
0·9678	23	0·9025	57	0·8199	91
0·9665	24	0·9001	58	0·8172	92
0·9652	25	0·8979	59	0·8145	93
0·9638	26	0·8956	60	0·8118	94
0·9623	27	0·8932	61	0·8089	95
0·9609	28	0·8908	62	0·8061	96
0·9593	29	0·8886	63	0·8031	97
0·9578	30	0·8863	64	0·8001	98
0·9560	31	0·8840	65	0·7969	99
0·9544	32	0·8816	66	0·7938	100
0·9528	33	0·8793	67		

Alcohol is converted by oxidising agents, such as manganese peroxide and sulphuric acid, chromic acid, finely-divided platinum and air, into *aldehyde*, C_2H_4O (*alcohol dehydrogenatus*), and into acetic acid.

The *proof spirit* is defined by law to be such as at the temperature of 51° F. shall weigh $\frac{12}{13}$ of an equal measure of distilled water. Taking water at 51° F. as unity, the specific gravity of "proof spirit" at 51° F. is 0·92308. When such spirit is raised to the more usual temperature of 60° F., the specific gravity is

0·91984. To calculate the quantity of spirits at proof in a given quantity of spirit over or under proof strength, multiply the quantity of spirit by the number of degrees of strength of the spirit, and divide the product by 100. The number of degrees of strength of any spirit is 100 plus the number of degrees overproof, or minus the number of degrees underproof. *Example.*—19·8 gallons of spirits at 64·5 overproof: 100 + 64·5 = 164·5 proof strength. 164·5 × 19·8 ÷ 100 = 32·571, taken as 32·5 gallons at proof.

Methylated spirit is exempted from excise duty. It contains chiefly ethyl alcohol, as also methyl alcohol and other substances, such as resins and $\frac{1}{3}$ per cent. of mineral naphtha, to make it unfit for drinking. Manufacturers can obtain it for industrial purposes without the addition of non-volatile substances.

Amyl Alcohol or Isobutyl Carbinol (*Fusel Oil*), $C_5H_{11}(OH)$, is the chief constituent of fusel oil, obtained in the rectification of potato spirit. It is a colourless liquid, possessing a peculiar penetrating smell; it dissolves in alcohol and ether, but is not miscible with water; one part only dissolves in 50 parts of water. The specific gravity is 0·8104 at 20° C., and the boiling point 132°. It yields on oxidation valeric acid. In its chemical properties amyl alcohol resembles ordinary alcohol.

Ether or Sulphuric Ether, $(C_2H_5)_2O$, is produced by heating a mixture of alcohol and sulphuric acid to 140° C. It is a colourless, very mobile liquid, possessing a strong and peculiar ethereal smell. It does not mix with water, but does so, in all proportions, with alcohol; it dissolves in ten parts of water. The specific gravity is 0·736 at 0° C. and the boiling point 35°. It evaporates rapidly at the ordinary temperature; and is very inflammable, burning with a non-luminous flame. When mixed with air it explodes, and, from its low boiling point, great care must be taken to avoid explosions.

Many organic compounds, notably hydrocarbons, fats, oils, and resins, readily dissolve in ether.

Ether is often used for removing stains from soiled pieces, and has the advantage over benzene and other solvents that it leaves no marks.

Glycerin, $C_3H_5(OH)_3$, is contained in most fats and fatty oils of the vegetable and animal kingdoms, and is formed in small quantities by the alcoholic fermentation of sugar. It is produced as a bye-product in the manufacture of soap and of stearin. Glycerin is a colourless syrupy liquid, which possesses a very sweet taste. It is very soluble in water and in alcohol, but insoluble in ether, and when anhydrous absorbs water from the air with avidity. It has a specific gravity of 1·265 at 15° C. It boils at the ordinary pressure at 290° with slight decomposition, and can be distilled without being decomposed at a reduced pressure, or in the presence of aqueous vapour.

Glycerin is a trivalent alcohol, and resembles ethyl alcohol in many respects. It dissolves the alkalies, alkaline earths, and many metallic oxides, probably forming compounds analogous to alcohol. It forms ethers with the inorganic and organic acids, the most important of which are the glycerin ethers of palmitic, stearic, and oleïc acid, which have been described in connection with the acids.

Glycerin is added on account of its hygroscopicity to print-colours, finishing materials, &c., to prevent them from drying.

Acetin is a mixture of the acetic ethers of glycerin (mono-, di-, and tri-acetin), and is produced by boiling glycerin with glacial acetic acid. It is a solvent for some dyestuffs—*e.g.*, the insoluble Indulines—and is used for this purpose in calico-printing.

Olive Oil.—Olive oil is produced from olives, the fruit of the olive tree (*Olea Europœa*, Linn), which is grown in southern countries. The ripe olives are ground to a pasty mass and pressed. The oil obtained from the first pressing—the so-called virgin oil (*huile vierge*)—is the best, and is used chiefly

as an edible oil. After the first pressing the material still retains much oil; it is treated with hot water and pressed once more. The oil obtained from the second pressing has a fine yellow colour, but it is more prone to become rancid than the virgin-oil. It is used for Turkey-red dyeing (*huile tournante*), and for oiling wool before spinning (*huile lampante*). By a third pressing an inferior oil is obtained, which is used for soap-making.

Olive oil consists chiefly of the tri-glycerides of oleïc acid, palmitic acid, and stearic acid, containing about 72 per cent. of oleïn, and 28 per cent. of palmitin and stearin.

The specific gravity of different oils varies from 0·914 to 0·917, but it rises to 0·920, and even to 0·925 in the case of hot-pressed oils which contain more palmitin or stearin. The oil becomes turbid at + 2° C., and at − 6° deposits 28 per cent. of palmitin and stearin.

Olive oil when exposed to the air, decomposes into free acid and glycerin, and becomes rancid—$C_3H_5(C_{18}H_{33}O_2)_3 + 3H_2O = C_3H_8O_3 + 3C_{18}H_{34}O_2$. It thus acquires a disagreeable smell and taste and an acid reaction. It is decomposed in the same way by the action of steam or by boiling with acids or caustic alkalies; in the last case salts of the acid are formed. At the ordinary temperature alkalies do not decompose the oil, although they form an emulsion with it (see below). *Gallipoli oil* or *emulsive oil* (*huile tournante*) is olive oil which contains free acids by having become rancid.

When olive oil is shaken well with a dilute solution of sodium carbonate a white milky liquid or an *emulsion* is formed; after some time two layers separate, one containing the oil, the other containing the aqueous liquid. If the oil contains free fatty acids they form a salt or "soap" with the caustic lye, and the presence of this soap tends to make the emulsion more permanent. The emulsion is merely a mechanical mixture of those parts of the oil which are insoluble in alkaline water (the undecomposed glycerides) with the caustic lye and the soluble products of decomposition (soaps). The oil exists in the emulsion in a state of the finest division, in which form it is particularly well absorbed by the cotton fibre. For this reason emulsive oil is extensively used in Turkey-red dyeing; the methods of application and the chemical reactions taking place in the fibre will be given under that heading. In calico-printing olive oil is used as an admixture to the printing colour for the purpose of making the paste smooth and free from air-bubbles. In silk dyeing it is largely used for softening the material after dyeing.

Castor Oil.—The seeds of *Ricinus communis* contain 40 to 45 per cent. of oil, which consists principally of triricinoleïn, the triglyceride of ricinoleïc acid, together with some stearin and palmitin.

Castor oil is a colourless liquid which possesses when fresh a mild, and afterwards an irritating taste; it is very viscous, and when exposed to the air gradually thickens to a tough mass. It does not dry completely, even in thin layers. The specific gravity is 0·960 to 0·964 according to Allen or 0·9613 to 0·9736 according to Valenta. It becomes solid between − 10° and − 18° C.

Pure castor oil mixes in all proportions with absolute alcohol and glacial acetic acid; it dissolves in two parts of alcohol of 90 per cent. strength, and four parts of alcohol of 84 per cent., but is insoluble in petroleum spirit.

Castor oil is saponified analogously to olive oil, the chief product being ricinoleïc acid.

Linseed Oil is obtained from the seeds of flax, *Linum usitatissimum*. It has a light yellow, or if obtained by hot pressing, a brownish-yellow colour and a peculiar smell and taste. The specific gravity at 15° C. is 0·930 to 0·935; it solidifies slowly at − 16° to − 27°. In the air it absorbs oxygen and soon becomes rancid and thick, drying in thin layers to a neutral substance which

is insoluble in ether. It is adulterated with fish oil, rape oil, hemp-seed oil, and cameline oil.

Linseed oil is chiefly used by painters on account of its property of drying and forming a varnish. For the same reason it is used in cotton-velvet dyeing. Prussian blue and other colours are mixed in a finely-ground state with linseed oil and painted on the velvet with brushes, in order to give it colour and a fine gloss.

Quillaya Bark.—This product, also known as soap bark, is imported from South America, and contains 8 to 9 per cent. of a peculiar glucoside known as *saponin*, having the composition $C_{32}H_{52}O_{17}$. The same compound occurs in soap root (*Saponaria officinalis*) and in other plant products. Being very soluble in water, saponin can be easily extracted from quillaya bark by boiling. It is a glucoside, and is hydrolysed by acids to sapogenin ($C_{14}H_{22}O_2$) and sugar. The aqueous solution froths strongly and, having emulsive properties, acts like soap as a detergent. It has a neutral reaction, and on this account it may in many cases find employment where soap could not be used. Quillaya bark (or its extract, saponin paste) finds extensive employment in cleaning (gloves, silks, &c.)., as a levelling agent in dyeing wool in light shades with acid colours, and in conjunction with fuller's earth in cleaning indigo-dyed woollen goods.

PART VI.

NATURAL COLOURING MATTERS.

INDIGO.

INDIGO has long been regarded as one of the most valuable and important of all colouring matters. It was used in India and Egypt long before the Christian era. It was introduced into Europe in the sixteenth century, but for a great many years very little was used on account of the opposition of the woad cultivators, who induced the English, French, and German governments to prohibit its use. The cultivators of woad contended that indigo was not only a fugitive dye, but that it was a corrosive and pernicious drug. In reality they feared that the importation of indigo would ruin their trade in woad. In France the law was so severe that Henry IV. issued an edict condemning to death anyone who used that "pernicious drug," which was called the "devil's food."

By far the greatest amount of indigo is obtained from India, and more especially from Bengal, Oude, and Madras. It is also manufactured in Java, Philippine Islands, China, Japan, Central America, Brazil, and certain parts of Africa. The principal plants cultivated for the manufacture of this dye are the *Indigofera sumatrana*, *Indigofera arrecta*, *Indigofera tinctoria*, *Indigofera anil*, *Indigofera disperma*, and *Indigofera argentea*. There are numerous other species of less importance.

Indigo is also obtained from other plants besides the genus *Indigofera*, but to a comparatively small extent. Among these may be mentioned the *Wrightia tinctoria* (cultivated to some extent in Madras), the *Strobilanthes flaccidifolius* (Assam), *Tephrosia toxicaria* (Bombay and Rajputana), the *Polygonum tinctorium* (China and Russia), *Lonchocarpus cyanescens* (West Coast of Africa), *Isatis tinctoria* (China, Afghanistan, &c.). The *Isatis tinctoria* or woad-plant was formerly largely cultivated in Europe, and was used exclusively up to the sixteenth century. It is still grown in Lincolnshire and on the Continent (South of France, Hungary, &c.), but is now never used alone for dyeing. It is employed in the fermentation vats in dyeing woollen goods. These vats are thus in consequence termed *woad-vats*. The woad assists the fermentation, and dyers further contend that it causes the indigo to penetrate more thoroughly into the interior of the fibre.

The cultivation and manufacture of indigo in Northern Behar have been described by Rawson in the *Journ. Soc. Chem. Industry* (May, 1899), and the *Journ. Soc. Dyers and Colourists* (July, 1899). A report to the Behar Indigo Planters' Association by the same author (printed at Mozufferpore, 1904), contains an account of the results of five years' experimental work in the cultivation and manufacture of indigo.

It has generally been stated that the plant grown in Bengal was *Indigofera tinctoria*, but according to Dr. Prain the plant is really *Indigofera sumatrana*, which was introduced into the province about 150 years ago.

In October, soon after the manufacturing season is at an end, the land is dug and thoroughly well ploughed. The preparation of the land is rather an elaborate process. The seed is sown by drills about the end of February or beginning of March. It germinates in the course of four or five days, and by the middle of June, when the manufacturing season usually commences, the plant has obtained a height of from 3 to 5 feet, and has a stem of about a quarter of an inch in diameter. The leaf of the plant is of a yellowish-green colour and shows no indication whatever of its containing anything productive of a blue colouring matter.

The leaf contains, on an average, about 0·5 per cent. of colouring matter; the variations are very great, ranging from about 0·3 to about 0·75 per cent. The colouring principle exists almost exclusively in the leaf. As the plant grows the colouring principle gradually increases until it reaches a maximum about the end of August. On the same plant new leaf is richer than old, and leaf near the top of a plant contains more colouring matter than that near the bottom. Refuse plant or "seet" is a very valuable manure, principally on account of the nitrogen which it contains. Applied to indigo lands it usually produces an excellent crop, but the leaf on such plant is invariably deficient in colouring matter. Far better results are obtained by applying refuse plant to land for other crops, and then growing indigo the following year. The best general manure for indigo is superphosphate of lime, though many soils in Behar already contain sufficient phosphoric acid. Numerous trials have been made in Behar with the Natal plant (*Indigofera arrecta*), and it is now being cultivated on a somewhat large scale. Many planters are very sanguine about the results. They anticipate that an acre of land will yield at least double the amount of indigo obtained from the ordinary plant.

Manufacture.—The manufacture of indigo in Behar is almost entirely carried out under the direction of Europeans. The manufacturing season usually commences about the middle of June, but it may be a fortnight earlier or a fortnight later. Soon after cutting, the plant throws forth fresh leaf, and after two or three months a second crop is obtained. The first and principal crop is called the "Morhan" crop, and the second the "Khoonties." The manufacturing seasons are spoken of as the "Morhan Mahai" and the "Khoontie Mahai" respectively. In some cases a week or a fortnight elapses between the two seasons; in others there is no break. The plant is cut early in the morning, often before daybreak, and taken to the factory in carts, each drawn by two bullocks. The work on an indigo "concern" is usually divided among a number of factories—from two to ten or twelve, according to the size of the concern. Each factory deals with plant grown within a radius of four or five miles. The principal part of an indigo factory consists of steeping vats and beating vats. The former are arranged on a higher level than the latter. Each steeping vat has a capacity of a little over 1,000 cubic feet. The actual dimensions are usually 18 feet by 16 feet by 3 feet 9 inches in depth, the depth being measured to the cross beams, and not to the top of the vat. Each range of beating vats runs the whole length of the steeping vats, and has a width of 13 feet 6 inches; a wall 3 feet high runs down the centre of the beating vat, but a space is left at each end so as to allow of a free circulation of the liquid when the wheel is set in motion. The beating wheel consists of a shaft armed with three sets of spokes. These spokes (six in number in each set) are furnished at the extremities with blades which, in revolving, churn up the liquid and cause a continual circulation. In some cases the steeping vat is divided into three parts, and the wheel works in the central division. The vats are built of brickwork faced with Portland cement. They are usually open to the air, though in some cases the steeping vats are covered. There are great variations in the arrangements of vats in different factories. In some

cases there are as many as eight steeping vats to one beating vat. The steeping vats are frequently arranged on each side of two or three ranges of beating vats, whilst in other cases the steeping vats are arranged in long rows with the beating vats alongside at a lower level. Formerly the steeping vats were much larger than at present, having a capacity of about 2,000 cubic feet, and each vat had a corresponding beating vat. The liquid was "beaten" by hand instead of by the wheel, and each vat required twelve coolies armed with beating sticks. In Madras and the North-West Provinces this method is still generally followed, and some factories in Behar have also a few hand-beating vats. In addition to the vats the requisite plant of an indigo factory includes a steam boiler and engine, pumps, boiling tanks, draining tables, presses, drying-house, and various workshops. On a higher level than the steeping vats a large water tank or "kajana" is situated. This is sometimes made of iron, but more usually it is constructed of brickwork and Portland cement, like the vats. The water is pumped into the "kajana" from the neighbouring river, stream or lake, and from it the steeping vats are filled.

Loading the Vats and Steeping.—In the first place, the vats are thoroughly cleansed; this is carefully done every day. A number of coolies enter the vat and scrub every part well, using a plentiful supply of water. The plant is then closely stacked in the vat in a more or less upright position, so as to allow the entangled air to escape more freely, and the liquid, after steeping, to drain away more completely.

The amount of green plant put into a vat of 1,000 cubic feet capacity varies from 11,000 to 15,000 lbs. When filled, a number of pieces of bamboo are placed across the top, and the whole kept in position by three or four stout pieces of timber fixed by iron pins running through racks attached to the sides of the vat. Water is now run into the vat until it reaches within a few inches of the beams. If filled completely, the liquid would subsequently overflow, as the plant undergoes a considerable expansion during the steeping process. A great pressure is thus exerted, and occasionally a beam is broken or the vat gives way. The length of time required for extracting the colour-yielding principle varies from nine to fourteen hours, according to the temperature and other climatic conditions. Ten to eleven hours may be considered a fair average period. The temperature of the water in June, July, and part of August is usually from 30° to 35° C., whereas in September it falls to about 27°, when a longer steeping is necessary. Whenever the temperature is under 32° C. it is advisable to heat the water in the reservoir to this point, or a little higher. This is decidedly preferable to prolonging the steeping operation. Indigo plant is not easily wetted by water, and for an hour or two no action takes place. After two or three hours the liquid rises in the vat, bubbles of air are liberated, and the surface becomes covered with a thick froth. Carbon dioxide is evolved in large quantities, and, in the later stages, either marsh gas or hydrogen, or a mixture of the two, is freely given off. If a light be applied to the surface of the vat towards the end of the steeping operation a blue flame extending for several yards may frequently be obtained. The vat has certainly the appearance of being in a state of active fermentation. After a time the liquid subsides, and this is the chief indication to the overseer, or the manager, that the plant is sufficiently steeped. The valve is now opened and the liquid run into the beating vat.

Beating.—The liquid running from the steeping into the beating vat varies in colour from a bright orange to an olive green, and possesses a peculiar fluorescence. When sufficiently steeped the liquid which runs out at first is of an orange colour, but it soon changes to a yellow and finally to an olive. When all the vats are discharged, the wheel is set in motion, at first slowly, and gradually increasing to a maximum. Under normal conditions from two

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to three hours are required to complete the operation of beating; although in some cases the length of time may be reduced to one or one and a-half hours. When nearing completion the froth, which at first was bluish, becomes white, and gradually disappears. In the meantime, the liquid changes through various shades of green to dark indigo blue. In order to ascertain when the beating is complete, a little of the liquid is poured on to a white plate. If the grain or "fecula" readily settles, leaving a clear fluid, the beating is considered accomplished, and the wheel is stopped. A better plan is to saturate a piece of filter paper with the solution, and subject it to the fumes of ammonia. If the slightest blue colouration is developed, it is an indication that the beating is not complete. In place of the beating wheel, various other devices for oxidising the liquid have been tried with more or less success. The most satisfactory method of oxidising indigo liquor is that of forcing a current of air through the solution. Either steam blowers or air compressors may be employed. For this purpose the beating vat is furnished with a number of rows of perforated iron pipes which lie at the bottom of the vat and are connected by means of a vertical pipe to the lower end of a steam blower or to an air compressor. When steam is admitted to the blower (or when the air compressor is put in motion) a powerful current of air is forced through the pipes and bubbles up through the liquid. It has the appearance of being in a state of violent ebullition, oxidation rapidly takes place, the indigo fecula settles more quickly and more completely than under the ordinary beating arrangements, and a greater yield of colouring matter is obtained. Many planters in Behar have adopted the process, and have obtained, on an average, an increase of about 20 per cent. compared with wheel beating.

After beating, the indigo "fecula" is allowed to settle, which usually takes two or three hours, when the supernatant liquid "seet water" is run off either by means of a surface drainer or by removing a series of wooden plugs arranged down the side of the vat. The bottom of the vat is inclined towards one corner where the precipitated indigo or "mal" is collected, passed through one or two strainers, whence it flows to a well, from which it is elevated, usually by means of a steam injector, to a large rectangular iron tank. The "mal" is strained again twice on its way from the well to the boiling tank. Every precaution is taken to keep the indigo clean and free from bits of twigs and dirt. The subsequent operations (boiling, pressing, cutting, and drying) of preparing indigo for the market are of a mechanical nature, and need not be described here.

The Colour-giving Principle and Solution obtained in Steeping.—It was formerly considered that indigo blue existed ready formed in the plant, and, at a later period, that it was present in the form of reduced indigo or indigo white. As long ago as 1850 Schunck, in his classical researches on the "Formation of Indigo blue," proved both these views to be incorrect. He found the leaves of certain indigo-yielding plants—the *Isatis tinctoria* and the *Polygonum tinctorium*—to contain a peculiar compound which he named *Indican.* Schunck showed that when leaves of the *Polygonum tinctorium* were placed in boiling alcohol, the colouring principle was entirely removed, and the leaf left of a yellowish-grey colour. When the vitality of the fresh leaf had been partially destroyed by being punctured or frozen, or treated with acid or cold spirits of wine, and then immersed in boiling alcohol, those portions which had been affected became blue, and the other portions were grey or colourless. Indican, which belongs to the class of bodies termed glucosides, is capable of being split up into indigo blue and glucose. It has recently been shown that this change does not take place directly, and that indican itself does not contain the molecule of indigo blue.

The glucoside present in leaves of *Indigofera sumatrana* does not appear to be identical with Schunck's indican, although closely resembling it. If a leaf

of *Indigofera* be crushed or bruised, the part does not (as in the case of *Isatis* and *Polygonum*) become bluish. On immersion in boiling alcohol the spot turns yellowish-brown.

Schunck and Römer * have shown that when indican is decomposed by hydrochloric acid in the absence of oxidising agents, a substance is produced which cannot be converted into indigotin; and further, that indigotin is formed from indican by the action of hydrochloric acid in the presence of an oxidising agent, and that these conditions—the presence of a hydrolysing agent and of an oxidising agent at the same time—are necessary for the production of indigotin. From the researches of these chemists, Marchlewski and Radcliffe † have propounded the theory that indoxyl was the parent substance or origin of indigotin, and that the glucoside, indican, on hydrolysis yielded glucose and indoxyl. Ranking, in a paper read before the Asiatic Society of Bengal in 1896, also states that the liquid after steeping probably contains indoxyl, and not indigo white, as had been formerly considered to be the case.

Whilst this part of the work was in the press an interesting paper on Indican by A. G. Perkin and W. P. Bloxam has appeared in the *Journal of the Chemical Society* (*Trans.*, 1907, p. 1715).

Much difference of opinion has prevailed as to whether fermentation is necessary for the production of indigo blue, or whether the fermentation is merely a result of the steeping process. It is possible to produce indigo blue from the plant under such conditions that bacteria could not exist, and this would tend to show that fermentation was not a necessity. On the other hand, Alvarez professes to have discovered the micro-organism which produces the indigo fermentation. He cultivated the microbe (named the *Bacillus indigogenus*), and found that it induced indigo fermentation in a sterilised extract of the leaves, which remained unaltered when freely exposed to the air without inoculation. Bréaudat ‡ attributes the formation of indigo to a "diastatic" fermentation, and not to the growth of a micro-organism.

C. Bergtheil § has shown that although there are several kinds of bacteria capable of producing the indigo fermentation, some of which are invariably present in an infusion of the plant, the action is in the main dependent on a specific enzyme occurring in the plant cells.

The liquid obtained on steeping the plant contains a number of substances —organic and inorganic—in solution, among which the most important, the indigo-forming principle, exists in very small proportion. An extract of indigo leaves has been variously stated to possess an acid, an alkaline, and a neutral reaction, but it has not been clearly stated what indicator was used for determining this condition.

Rawson found a fresh decoction of the plant to be neutral to both red and blue litmus paper. It was decidedly alkaline to Methyl orange, and acid to phenolphthalein. The liquid contains a large amount of lime, magnesia, and potash, chiefly in combination with carbonic and organic acids. The solution obtained in steeping contains on an average about 0·55 per cent. of dry solid matter. This amount corresponds to 55 lbs. per 1,000 gallons. Nearly one-half of the total solids consists of mineral matter, bicarbonates of lime, magnesia, and potash predominating. The bulk of this matter, and practically the whole of the colouring matter, is derived from the leaves. Even the fine stems yield but traces of colour. The indigotin only equals about $\frac{1}{25}$ part of the total matter extracted from the plant. The average amount of indigo produced on a manufacturing scale per 100 lbs. of plant is about 4 ozs., but the figures vary greatly in different factories, and also at different times in the same factory.

* *Ber. d. deut. Chem. Ges.*, 1879, p. 2311.
† *Journ. Soc. Chem. Ind.*, May, 1898.
‡ *Comptes Rendus*, 1898, p. 769.
§ *Journ. Chem. Soc.* (*Trans.*), 1904, p. 870.

Effect of Alkalies.—When an alkaline body, such as lime, soda, or ammonia is added to indigo liquor, carbonic acid (free and as bicarbonate) is neutralised, and calcium and magnesium carbonates are precipitated. The solution thus treated is much more readily oxidisable by air than it was before the addition, and, if the oxidation is carried out without delay, an increased amount of indigotin is invariably obtained. Lime has been largely used, but, except under special conditions, there are many objections to its use. The most successful method of applying lime was that introduced by Coventry. In this case the great bulk of precipitated carbonates and insoluble impurities are removed by subsidence in a special vat placed between the steeping and beating vats. Each steeping vat has a corresponding precipitating vat. The requisite amount of lime is placed in a small tank or box fixed just above the outlet of the steeping vat. It is mixed with water, and the milk of lime thus formed is allowed to run into the precipitating vat simultaneously with the liquor run out of the steeper. If mixed afterwards, oxidation takes place and indigo is lost. The precipitate produced and the impurities in the lime soon settle, and after half an hour or so the supernatant liquid is run off into the beating vat and treated in the usual way. Oxidation takes place rapidly, and usually in the course of about half an hour the beating operation is complete. Although the great bulk of the lime is left in the "precipitator," in some cases the indigo produced by this process contains a large amount of mineral matter, chiefly lime. For the successful working of the operation it is, therefore, necessary to use an acid. Coventry adds the acid to the "mal" in the boiler, after running off as much of the clear waste water as possible. The exact amount of acid necessary may be determined by means of blue litmus paper. The indigo obtained by this process is of very high quality, and it usually contains a high percentage of indirubin or indigo red. Caustic soda and ammonia both give excellent results, and in either case the ordinary arrangement of vats may be retained. Of all alkaline reagents hitherto tried, ammonia, in the form of gas (Rawson's process), has given the best results. It finds special application when steam blowers or air compressors are used for oxidising indigo liquor, though it may be applied to any form of beating. Indigo produced by this process is of fine and regular quality. Neither yield nor quality is influenced by unfavourable climatic conditions, which have so great an effect upon both when the ordinary process of manufacture is followed.

Constituents of Indigo.—Indigotin is by far the most important constituent of natural indigo. Its proportion varies greatly, from 5 to 90 per cent. Good Bengal indigo may be said to contain on an average from 60 to 66 per cent. Madras indigo, on the whole, is of inferior quality. It contains on an average about 30 per cent., but the variations are much greater than in the case of Bengal indigo. Some qualities contain upwards of 50 per cent. Broadly speaking, the indigo made in the North-West Provinces (Oude, &c.) is of a quality intermediate between that of Bengal and Madras. Java indigo contains, as a rule, the highest percentages of indigotin, but the general opinion of woollen dyers in England is that it does not give such good results as a high-class Bengal product of a corresponding quality. Indigo also contains another colouring matter—viz., indirubin or indigo red. Until comparatively recently this constituent was rarely present beyond 2 per cent., but at the present time commercial indigo frequently contains as much as 10 per cent. and upwards.

In addition to indigotin and indirubin, natural indigo contains a variety of other substances which are usually regarded as impurities, though in some cases the organic matters have an appreciable effect in dyeing. They comprise indigo gluten and various brown substances, and amount in all to about 20 to 30 per cent. Natural indigo always contains more or less mineral matter.

This is partly derived from the leaves of the plant, and partly from suspended matter (clay and sand) present in the water used for steeping. The amount of mineral matter found in natural indigo varies greatly from 2 or 3 per cent. to 60 per cent., and even more. Good Bengal indigo usually contains from 3 to 6 per cent.

Indigotin, $C_{16}H_{10}N_2O_2$, may be prepared from natural indigo in a variety of ways. It is, however, very difficult to remove the last traces of impurity. A method which gives very good results is known as Fritzsche's process, and may be performed in the following manner:—5 grammes of very finely-powdered indigo, 10 grammes of pure grape sugar, 50 c.c. of a 40 per cent. solution of caustic soda, 150 c.c. of water, and 300 c.c. of 90 per cent. alcohol are put into a flask fitted with a cork and syphon tube. The mixture is heated on a water-bath for half an hour, and the insoluble matters are allowed to subside. The clear liquid is syphoned off, and a current of carbon dioxide passed through it, and then a current of air. Indigotin is thereby precipitated; it is collected on a filter, washed (1) with dilute hydrochloric acid, (2) with water, and then dried. The dried product is further purified by crystallisation from boiling glacial acetic acid. Indigotin of a high state of purity is best obtained from synthetic indigo which already contains about 98 per cent. of the pure substance. Indigo pure, in powder, is boiled several times with a 10 per cent. solution of pure sulphuric acid, and well washed with hot water. It is now reduced with hydrosulphite and caustic soda. The filtered solution is oxidised by a current of air, and the washed precipitate boiled successively with dilute hydrochloric acid and alcohol. After drying, the product is crystallised out from boiling glacial acetic acid, and the crystals washed with alcohol and ether, then with hot dilute hydrochloric acid, and finally with water. The crystals are now dried at 105° C.

Pure indigotin crystallises in beautiful dark blue or purple needles, which exhibit a coppery reflex. The powder, which is of a deep blue colour, assumes a bright red bronzy appearance when burnished. Indigo begins to sublime, according to Schunck, at 170° C., but other authorities give a much higher subliming point. The vapour possesses a beautiful red-violet colour, resembling that of iodine. In the open air, although the greater portion of the indigotin sublimes, it is partially decomposed, leaving a mass of porous carbon. In an inert gas it may be volatilised without decomposition. When submitted to dry distillation—that is, heated in a closed vessel either alone or with an alkali—indigotin is decomposed, the chief product being aniline.

Indigotin is a neutral body, and is insoluble in water, ether, dilute acids, and alkalies. It is slightly soluble in boiling alcohol with a blue colour, but is again deposited on cooling. Amylic alcohol, carbolic acid, chloroform, and carbon bisulphide also dissolve small quantities when hot, but the best solvents for indigotin are glacial acetic acid, nitrobenzene, quinoline, and aniline. Boiling paraffin dissolves indigotin with a magenta colour. Concentrated sulphuric acid completely dissolves indigotin, but, since its composition is changed, sulphuric acid cannot be considered a solvent for indigotin as such. Glacial acetic acid containing a few drops of sulphuric acid, dissolves indigotin with a deep blue colour, and dilution with water reprecipitates it unaltered.

By the action of oxidising agents, such as dilute nitric acid, chromic acid, &c., indigotin is converted into *isatin*. If nitric acid is used hot, it forms nitro-salicylic acid or Picric acid, according to the strength of the acid. At the same time other products, such as carbonic acid and oxalic acid, are formed.

If indigotin is heated from 80° to 85° C. with hydrosulphite of soda rendered alkaline by caustic soda for 48 hours, the solution deposits a

precipitate from which alcohol extracts a body having the composition $C_{32}H_{22}N_4O_4$, while indigotin remains in the residue.* This substance, which is of a dark-red colour, dissolves in alkalies with a green colour. On boiling, the solution becomes yellow, and acids then separate a yellow precipitate of *flavindine*, $C_{32}H_{24}N_4O_5$, which yields *indoline* when heated with zinc powder.

When indigo white is heated with zinc powder and an aqueous solution of barium hydrate to 82° C., it is reduced to indoline † or di-indol, $C_{16}H_{14}N_2$, which sublimates on heating in long, pale yellow needles, and melts at 118° C. It is insoluble in water, but soluble in alcohol and in ether with a blue fluorescence. It combines with acids. Titanous chloride apparently produces a similar compound when finely-divided indigo is boiled with the solution.

Reduced Indigo or Indigo White.—By the action of certain bodies, termed "reducing agents" (compounds capable of giving up nascent hydrogen or assimilating oxygen), indigotin is converted into a colourless compound known as *indigo white* or *reduced indigo.* This body is soluble in dilute alkaline liquids, such as lime, potash, or soda. It is in this form that indigo is used for dyeing. The material to be dyed is immersed in a vat containing reduced indigo; this, on exposure to the air, is oxidised to indigotin, which is thus fixed in the insoluble form on the fibre.

There are numerous substances which have the power in alkaline solution of reducing indigo blue to indigo white—*e.g.*, sodium amalgam, zinc, tin, aluminium, magnesium, &c.; ferrous hydrate; hydrosulphurous and hypophosphorous acids; sulphide of arsenic, &c.; glucose, gallic acid, &c.; and certain organic ferments. From a hydrosulphite vat containing an insufficient amount of alkali, indigo white is deposited in the form of minute, glittering, silvery-white crystals. In an amorphous state it is a greyish-white powder, insoluble in water and dilute acids, but soluble in alcohol and ether, and in alkaline solutions; the powder on exposure to air oxidises to blue indigotin; the change rapidly takes place in the presence of water. An alkaline solution of reduced indigo has a brownish-yellow colour; an excess of reducing agent gives a clear, bright yellow solution. On exposure to the air it becomes at first green, then blue, and is covered with a bronzy scum, which consists of minute crystals of indigotin. If an oxidising agent, such as potassium bichromate, be added to the solution, the blue colour of indigotin is at once developed. An alkaline solution of reduced indigo gives bulky white precipitates with salts of alumina, zinc, magnesia, and the proto-salts of iron, lead, and tin. The tin compound was formerly used in calico-printing.

Indigotin Sulphonic Acids.—It has been already stated that indigotin dissolves in concentrated sulphuric acid, thereby undergoing a change in its composition. According to the conditions either mono- or disulphonic acid is formed. By the action of fuming sulphuric acid, tri- and tetra-sulphonic acids are formed.

Indigotin monosulphonic acid, also known as sulphopurpuric acid and indigopurpuric acid, is obtained by mixing 1 part of indigotin with 4 parts of concentrated sulphuric acid, and allowing the mixture to stand not more than half an hour, when it is diluted with water. A beautiful purple precipitate is formed which is only sparingly soluble in water. The sodium salt is used in dyeing under the names of indigo purple, red extract of indigo, and red indigo carmine.

Indigotin disulphonic acid, also known as sulphindigotic acid, is obtained by treating indigotin with a larger proportion of sulphuric acid and allowing it

* Giraud, *Bull. Soc. Chim. de Paris*, xxxiv., p. 530.
† Schützenberger, *Jahresber*, 1887, p. 511.

to act for a longer time, or by heating the mixture, or both combined. One part of indigotin treated with 10 or 12 parts of concentrated sulphuric acid at a temperature of 90° C. is converted into the disulphonic acid in about half an hour. At the ordinary temperature it is necessary to allow the mixture to stand for 10 or 12 hours. On diluting with water the sulphonic acid remains in solution, being soluble in about 60 parts of water. If any monosulphonic acid is present, it is precipitated in the form of a purple powder. The pure sulphonic acid may be obtained by adding a saturated solution of common salt which produces a precipitate of sodium disulphonate. The precipitate is collected on a filter and washed with a saturated solution of salt in order to remove free acid. The paste is then dissolved in water and the solution precipitated by lead acetate. The insoluble lead salt is washed and decomposed by sulphuretted hydrogen. The solution freed from lead sulphide, yields on evaporation pure indigodisulphonic acid. It is insoluble in alcohol.

Indigodisulphonic acid is decolourised by reducing agents in a similar manner to indigotin itself. The colourless solution becomes blue again on exposure to air. By the action of oxidising agents, such as potassium bichromate, and potassium permanganate, it is converted into isatin disulphonic acid. Both these series of reactions are utilised for the estimation of indigotin in commercial indigo.

Indigodisulphonic acid when treated with strong solutions of caustic alkalies, forms at first a green and ultimately an orange-coloured solution. Weak solutions and alkaline carbonates form disulphonates, which are soluble in water, but very sparingly soluble in strong saline solutions.

The potassium salt dissolves in about 150 parts of water, and the sodium salt is somewhat more soluble. The lead salt is insoluble, and the barium salt is only very sparingly soluble. The sodium salt is sold as Indigo carmine.

Strong ammonia added to a solution of sodium disulphonate produces a green colour, which is named by V. H. Soxhlet,* Indigo green. The product has not been thoroughly investigated. It may be simply a mixture of disulphonate and some yellow decomposition product.

Indigodisulphonic acid may be prepared synthetically by the action of fuming sulphuric acid on phenylglycine.†

Indigotin tri- and tetra-sulphonic acids have been prepared and examined by W. P. Bloxam.‡ They are formed by the action of fuming sulphuric acid on indigotin. He makes use of the tetra-sulphonic acid in purifying commercial indigo for analysis.

Indirubin, or *Indigo red,* is isomeric with indigotin, $C_{16}H_{10}N_2O_2$. It has been previously stated that when indican, the glucoside existing in woad, and probably in the *Indigoferæ,* is submitted to fermentation or treated with dilute acids, it splits up into indigotin and sugar. This indican is very susceptible of alteration, and its modifications yield, according to existing conditions, either indirubin or indiretin and indihumin, the latter two bodies forming indigo brown. Schunck found that when indican was mixed with caustic soda and allowed to stand for some days, the solution yielded indirubin, but no indigotin. Indican thus modified by the action of caustic soda was named by Schunck *indicanin.*

Whenever an alkali is used in the manufacture of indigo, a greater amount of indirubin is formed than under ordinary conditions, and the proportion increases according to the time allowed to elapse before oxidising the liquor.

Indirubin may be obtained from commercial indigo by extraction with alcohol or ether, indigotin being insoluble. The indigo should, in the first

* *Chem. News,* lxiv., p. 85. † Heymann. *Journ. Soc. Chem. Industry,* 1891, p. 827.
‡ *Journ. Soc. Chem. Ind.,* 1906, p. 736.

case, be boiled with dilute hydrochloric acid, and washed with water. A hot concentrated solution of indirubin in alcohol deposits the indirubin on cooling in the form of microscopic bundles of dark purple-coloured needles. Indirubin sublimes at a lower temperature than indigotin, and condenses again in the form of beautiful crimson needles. It is unaffected by weak acids and alkalies, but, like indigotin, is reduced to a colourless compound soluble in alkalies by the action of substances yielding nascent hydrogen. Wool or cotton immersed in such a solution and then exposed to the air becomes dyed a fast purple colour. Indirubin dissolves in concentrated sulphuric acid, forming a deep crimson solution, which produces no precipitate on dilution with water. This solution is oxidised but slowly by potassium permanganate or bichromate. If solutions of indigotin- and indirubin-sulphonic acids be mixed together and titrated in the cold with potassium permanganate the whole of the blue compound is decomposed (decolourised) before the red is affected. On slowly continuing the addition of potassium permanganate the colour of the solution passes from a crimson to bright scarlet, and then through various shades of orange to a bright yellow.

Indirubin itself is unaffected when boiled with a mixture of potassium bichromate and sulphuric acid, whereas indigotin is decomposed.

Indirubin dyes wool and cotton crimson shades which are exceedingly fast to light. The sulphonic acid of indirubin dyed on wool from an acid bath is far faster than the corresponding indigotin compound.

Notwithstanding the fastness of shades dyed with indirubin, this colouring matter, contrary to much which has been written in its favour, has very little value as a dye. Recent experiments have shown that in the vat indirubin is partially more or less quickly converted into indigotin, whilst other portions are destroyed with the formation of worthless brown and yellow colouring matters. These changes take place particularly quickly in the zinc-lime vat; but they also occur, at a less rapid rate, in hydrosulphite and other vats.

Indigo Brown.—The brown substances present in indigo are named by Schunck *indiretin* and *indihumin*. When a solution of indican is heated for some time and then treated with an acid, it yields neither indigotin nor indirubin, but a dark brown precipitate consisting of these two bodies, which are invariably present to a greater or less extent in commercial indigo.

The brown matter dissolves in caustic soda, and a portion of it is precipitated on neutralising the liquid with an acid. It dissolves in concentrated sulphuric acid with a deep dark brown colour, but is almost entirely precipitated on dilution with water. Schunck* describes the formation of five brown compounds derived from indigo blue.

In the manufacture of indigo, more brown compounds are formed at the expense of indigo the longer the liquor is allowed to stand before oxidising.

The brown matters in natural indigo have recently been studied by A. G. Perkin and W. P. Bloxam.†

Yellow Colouring Matter.—In recent years Java indigo has frequently been found to contain a yellow substance‡ which interferes greatly with the ordinary methods of estimating indigotin.

This substance is almost insoluble in water and dilute acids, but dissolves in concentrated sulphuric acid, and remains in solution on dilution with water. On the addition of salt to this solution, a precipitate is obtained which is soluble in water. It is soluble in glacial acetic acid. The compound dissolves readily in alkaline solutions with a deep yellow colour; on the addition of

* *Memoirs of the Lit. and Phil. Soc. of Manchester*, 1864-5.
† *Journ. Chem. Soc. (Trans.)*, 1907, p. 279.
‡ Rawson, *Journ. Soc. Chem. Ind.*, 1899, p. 251.

dilute acids it is thrown down as a pale yellow flocculent precipitate. It is soluble in alcohol and ether. The solution is colourless, but a trace of alkali produces a deep bright yellow. On the application of a gentle heat the substance melts, partially sublimes, giving off dense, yellowish-white vapours, and leaves a mass of carbon. Although nearly insoluble in water, it dyes wool mordanted with bichromate of potash a good yellow shade, resembling that given by weld or vine leaves. It does not dye unmordanted wool, hence it is a mordant colour.

The same yellow compound was also found in the leaves of several samples of indigo plant grown in Bengal* from Natal-Java seed. New leaves were particularly rich in this colour, but in old plants very little was found.

A. G. Perkin† has made a careful study of this compound and has established its identity with kaempferol.

Synthetic Indigo.—After many years of labour, artificial indigo was introduced into the market under the name of "Indigo pure" in July, 1897, by the Badische Anilin- und Soda-Fabrik. Indigotin had previously been produced synthetically in a variety of ways, but the cost of production was far above that of the natural product. Baeyer's name will always remain inseparably connected with the synthesis of indigo. In 1870 Baeyer and Emmerling succeeded in producing indigotin from isatin, but the synthesis was not complete until 1878, when the former chemist obtained isatin from indoxyl, and in conjunction with Suida prepared, in its turn, indoxyl from orthoamidophenylacetic acid. In 1880 Baeyer obtained indigotin in various ways from cinnamic acid.

One method may be briefly summarised as follows:—

(*a*) Formation of orthonitrocinnamic acid.

(*b*) Treatment with bromine whereby orthonitrodibromhydrocinnamic acid is produced.

(*c*) By action of caustic alkali orthonitrophenylpropiolic acid is obtained.

(*d*) Reduction with glucose or xanthates when indigotin is formed.

In 1882 Baeyer and Drewsen obtained indigotin from orthonitrobenzaldehyde by treating this compound with acetone or acetic aldehyde in the presence of caustic alkali. In this reaction orthonitrophenyl lactone is formed as an intermediate product. In 1893 Kalle & Co. introduced their "Indigo salt," which consists of the above-named body in combination with sodium bisulphite. It is readily soluble in water, and yields indigotin at once on the addition of caustic soda.

In 1890 details of Heumann's synthesis of indigo from phenylglycocol were published. When heated with caustic alkalies to a temperature of 250° C. phenylglycocol is converted into pseudoindoxyl, which, on oxidation, yields indigotin. This process, together with several others for the production of indigotin and intermediate compounds, is in the hands of the Badische Anilin- und Soda-Fabrik. The development of Heumann's synthesis into a practical technological process has been described by Dr. Brunck in a lecture given to the German Chemical Society on the 20th October, 1900. The starting point of this synthesis is naphthalene, which is converted into phthalic acid by heating it with highly concentrated sulphuric acid in the presence of mercury. For every pound of naphthalene oxidised about 4½ lbs. of sulphur dioxide are evolved, so that the whole success of the process is dependent on the effective recovery of this compound. The sulphur dioxide is converted into fuming sulphuric acid by the contact process, and used over and over again. From phthalic acid, indigotin is produced in the following stages:—

* C. Rawson, *Report on the Cultivation and Manufacture of Indigo*, 1904.
† *Journ. Chem. Soc.*, 1907, p. 435.

1. $C_6H_4\begin{cases}COOH\\COOH\end{cases}$

Phthalic acid.

2. $C_6H_4\begin{cases}CO\\CO\end{cases}>NH$

Phthalimide.

3. $C_6H_4\begin{cases}COOH\\NH_2\end{cases}$

Anthranilic acid.

4. $C_6H_4\begin{cases}COOH\\NHCH_2COOH\end{cases}$

Phenyl-glycin orthocarboxylic acid.

5. $C_6H_4\begin{cases}CO\\NH\end{cases}>CH_2COOH$

Indoxyl carboxylic acid.

6. $C_6H_4<{CO \atop NH}>C=C<{CO \atop NH}>C_6H_4$

Indigotin.

Synthetic indigo possesses the same chemical and dyeing properties as indigotin from natural indigo. The two products are identical.

Indirubin, like indigotin, can also be made synthetically, and has been put on the market to a limited extent by the Badische Anilin- und Soda-Fabrik. Baeyer obtained it by the action of indoxyl on isatin, and it is also produced along with indigotin by the reduction of isatin chloride.

The constitution of synthetic indirubin was first established by Baeyer, but the formula he proposed has since been slightly altered by Schunck and Marchlewski. These chemists have shown* natural and artificial indirubin to be identical.

Later, Marchlewski and Radcliffe† have found synthetic and natural indirubin to behave in exactly the same manner under similar conditions. They also found that indirubin was only partially converted into indigotin in the presence of *alkaline* reducing agents, whereas complete conversion took place when it was treated with acid reducing agents.

The Farbw. vorm Meister, Lucius & Brüning, as well as the Badische Anilin- und Soda-Fabrik, now manufacture enormous quantities of synthetic indigo. Each firm makes numerous brands for use in particular cases, but the chief forms are powder (of about 98 per cent. purity) and 20 per cent. paste. Brom-indigo is a well known brand and dyes redder shades than the ordinary kind. In the section "Application of Indigo," the recipes generally refer to 60 per cent. Bengal indigo, but synthetic may be in all cases substituted in the following ratio:—

10 parts, . .	60 per cent. Bengal indigo.
6 ,, . .	Indigo pure powder.
30 ,, . .	Indigo pure 20 per cent. paste.

Application of Indigo.—Indigo is a substantive dye, and consequently requires no mordant. It is used very largely both in wool and cotton dyeing. In addition to the dyeing and printing of blues, indigo is used to a very great extent as a bottom for compound shades. Such shades, browns, olives, blacks, &c., which contain indigo are said to be *woaded*. In most cases the cloth or other material is dyed with indigo first and then filled up (mordanted, if necessary) with the other colouring matters. In any case, the indigo requires a special vat. As previously stated indigo is applied to the textile fibres in the form of indigo white or "reduced indigo" soluble in alkalies. Many of the substances, already mentioned as being capable of transforming indigo blue into indigo white, are utilised on the large scale for the dyeing of indigo. For the dyeing of wool the vats are usually heated to a temperature of about 50° C. Cotton and other vegetable fibres are generally dyed cold.

The following are the most important indigo vats:—

* *Berl. Ber.*, 1895, p. 539.

† *Journ. Soc. Chem. Ind.*, 1898, p. 434.

Woad vat.
Soda or German vat.
Potash vat. — **used in wool dyeing.**
Urine vat.
Hyposulphite or "hydrosulphite" vat.
Copperas vat. — **used in cotton dyeing.**
Zinc vat.

Dyeing of Cotton.—The principal vats for cotton are the hydrosulphite, the copperas, and the zinc vat.

Hydrosulphite Vats.—Sodium hydrosulphite was first recommended by Schützenberger and Lalande for reducing indigo, and is now very largely used in the dyeing of both wool and cotton. Hydrosulphite vats may be prepared either with lime or caustic soda. In either case a stock or standard vat should be prepared apart from the actual dyeing vat. In England the hydrosulphite-lime vat is used to a greater extent than the corresponding soda vat, and more particularly for the dyeing of wool, though it is also largely used for cotton yarn, &c. In the dyeing of cotton more lime and less hydrosulphite are required than for wool. The strong solution of reduced indigo may be conveniently prepared in a cask holding about 50 gallons in the following manner:—20 lbs. of 60 per cent. indigo, thoroughly well ground to a smooth paste, are put into the cask with about 20 gallons of boiling water and mixed with milk of lime containing 24 lbs. of quicklime. In the meantime 7 gallons of bisulphite of soda (52° Tw.) have been slowly mixed with 7 lbs. of good zinc dust. In about a quarter of an hour the mixture will have become of a light greyish colour and will have lost its smell of sulphurous acid. It is then added to the mixture of indigo and lime, and the cask filled with hot water so as to bring the whole to a temperature of about 80° C. The mixture is well stirred and the cask covered to exclude air. It is allowed to stand, with occasional stirring, for about two hours, when the mixture will have acquired a deep yellow colour and is ready for use. In dyeing, the vat is filled with water and a small quantity of hydrosulphite solution or mixture of bisulphite and zinc is added (with a little milk of lime) to remove free oxygen. After half an hour or so the necessary amount of reduced indigo solution, according to shade required, is added, the vat well stirred, and allowed to stand for about an hour for the insoluble matters to settle. The dyeing may then be commenced.

The *hydrosulphite-soda* vat possesses several advantages over the corresponding lime vat. In the first place, the vat contains little or no sediment, and the goods do not require acidifying after dyeing. There is considerably less indigo wasted. This vat is particularly adapted for dyeing piece goods. A standard indigo solution of a similar strength to that above described may be prepared as follows:—20 lbs. of 60 per cent. indigo, thoroughly ground to a smooth paste, are put into a cask with about 15 gallons of boiling water, and mixed with 7 gallons of caustic soda solution (42° Tw.). To this mixture 18 gallons of hydrosulphite solution are added with sufficient hot water to bring the whole up to 50 gallons. The temperature is maintained at about 70° C. for one to two hours. The condition of the vat may be ascertained by dipping into it a strip of sheet glass. When completely reduced the liquor running from the strip of glass is yellow and takes about half a minute to turn green.

The hydrosulphite solution used in preparing this vat is made in the following manner:—10 gallons of bisulphite of soda (52° Tw.) are mixed with 15 gallons of cold water, and 8 lbs. of zinc powder (made into a paste with a gallon of water) are slowly added with cautious stirring. After about an hour 2 gallons of milk of lime (containing 10 lbs. of quicklime) are added to the mixture, and the whole stirred for some time and then allowed to stand for two to four hours. It is finally filtered, preferably by means of a filter press. The

hydrosulphite solution should be used as soon as possible, and should never be left exposed to the air. In preparing a vat for dyeing, hydrosulphite solution, in the proportion of about 1 gallon to 500 gallons of water, is added in the first place, and then, after standing at least an hour, the requisite amount of prepared indigo solution according to the depth of shade to be dyed.

The Badische Anilin- und Soda-Fabrik have recently introduced hydrosulphite in the form of powder, which greatly facilitates the preparation of hydrosulphite dye vats. Hydrosulphite powder possesses the great advantage over all other hydrosulphite preparations in being much more concentrated and at the same time quite stable. In working with liquid hydrosulphite there is always a considerable loss, even under the most favourable conditions, and if indigo vats are only used occasionally, the loss may reach an enormous proportion. This is entirely avoided by the use of hydrosulphite powder.

The Badische Anilin- und Soda-Fabrik recommend the following proportions:—10 lbs. of Indigo pure 20 per cent. paste are mixed with 2 gallons of cold water; $2\frac{1}{2}$ lbs. hydrosulphite powder are slowly added during constant stirring for about ten minutes, when 5 pints of caustic soda solution (76° Tw.) are added. The mixture is now heated for one to two hours until the liquid running from a strip of sheet glass shows complete reduction. In place of 10 lbs. of Indigo paste (20 per cent.), $3\frac{1}{3}$ lbs. (60 per cent.) natural indigo may be taken, the quantities of the other ingredients remaining the same. In preparing a dye-vat about 1 oz. hydrosulphite powder should be added per 100 gallons of water to remove free oxygen.

Copperas or Ferrous Sulphate Vat.—This vat, which forms one of the oldest methods of indigo dyeing, is made up with copperas, lime, and indigo. The lime decomposes the ferrous sulphate, forming calcium sulphate and ferrous hydrate, and the latter, having a great tendency to absorb oxygen and pass into ferric hydrate, decomposes water liberating hydrogen. The hydrogen is not given off as gas, but immediately combines with the indigotin to form indigo-white, which dissolves in the excess of lime present. The amounts of indigo, lime, and copperas vary according to the work to be done, and the order in which the ingredients are added varies with different dyers. The following figures give a general idea of the proportions of indigo, copperas, and lime required for setting a vat:—

Water,	200 gallons.
Indigo (60 per cent.),	10 lbs.
Copperas,	30 "
Quicklime,	35 "

Some dyers add these substances direct to the dye vat, but it is much better to mix them previously in a more concentrated form, and to accelerate the reaction by the aid of heat. A cask furnished with a lid answers the purpose well. The 10 lbs. of indigo, ground thoroughly well to a smooth paste, is mixed with 8 gallons of water at 65° C. Milk of lime (containing 35 lbs. quicklime) of the same temperature is added during constant stirring, and this is followed by the 30 lbs. of ferrous sulphate dissolved in about 10 gallons of hot water. More water, at a temperature of 60° to 65° C., is added until the whole measures about 50 gallons. The lid is put on the cask and the mixture allowed to stand (stirring occasionally) for three to four hours, by which time the liquor will have assumed a fine amber yellow colour. The mixture may then be poured into the dye vessel which has been already three parts filled with water, stirred up, and allowed to settle. Before entering the goods, the flurry is removed by means of an iron scoup called a *skimmer*.

The "copperas" vat is used chiefly for hank and "resist" dyeing. It is not suitable as a continuous vat. It is usual to have several vats of different

strengths, the white yarn being put into the weakest vat, and then into the stronger ones. Three to six dips are frequently given in successively stronger vats. The vat mentioned above is a comparatively strong vat. Weaker vats should be prepared (when old partially exhausted vats are not available) by taking one-half and one-quarter of the amount of indigo respectively. With weaker vats it is advisable to slightly increase the proportion of lime and ferrous sulphate. In the preparation of a set of three vats, the following figures may be given as a guide:—

	Strong Vat.	Medium Vat.	Weak Vat.
Water, ...	200 gall.	200 gall.	200 gall.
Indigo (60 per cent.), . .	10 lbs.	5 lbs.	2½ lbs.
Copperas, ...	30 ,,	18 ,,	11 ,,
Quicklime, ...	35 ,,	20 ,,	11 ,,

A copperas vat always contains a large amount of a bulky sediment which causes a considerable loss of dyestuff. Before dyeing sufficient time must always be given for the vat to settle well, otherwise finely-divided hydrated oxides of iron fix themselves on the fibre and produce disagreeable shades. The copperas vat has been largely replaced by the hydrosulphite and zinc-lime vats.

The Zinc-lime Vat.—This vat is extensively used in continuous dyeing machines, both for cotton warps and piece goods; in the latter case particularly for discharge printing. It is also used for "resist" prints and for yarn dyeing. It is a comparatively simple vat, the working of it depending on the property of zinc powder reacting on slaked lime to form calcium zincate and hydrogen. In the presence of indigo the hydrogen, instead of being liberated as gas, reduces the indigotin to indigo white, which dissolves in the excess of lime forming a vat. This is a very simple view of the principle of the vat, but the actual changes which occur are no doubt much more complex. The vat possesses several advantages over the copperas vat. It contains but little sediment, and, even if not quite clear, the shades obtained are not affected in the same way as those dyed in a muddy copperas vat.

The ingredients are often added direct to the dye-vat, and the reduction allowed to take place at the ordinary temperature; but it is far preferable to prepare the solution in a more concentrated form, at a higher temperature. At about 50° C. reduction is complete in four to five hours, and there is much less loss of indigo than takes place with the slow reduction at the ordinary temperature.

As mentioned under the preparation of a copperas vat, a cask with a well-fitting lid forms a suitable vessel for preparing the standard solution of reduced indigo. For a vat of 400 gallons capacity the standard solution might be prepared as follows:—16 lbs. of 60 per cent. indigo, well ground with water into a smooth paste, are mixed with 8 lbs. of zinc powder, made into a thin paste, with 8 gallons of water. To this mixture milk of lime (containing 20 lbs. of quicklime), at a temperature of 50° C., is added, and the whole made up to about 30 gallons, with water at 50° C. The mixture is well stirred, covered, and allowed to stand, with occasional stirring, for about four hours, when, if in good order, it will have acquired a fine yellow colour, and be ready for use. In the meantime the dye-vessel has been nearly filled with water, and sharpened with 1 lb. of zinc powder and 2 lbs. of lime. The solution of reduced indigo, with solid matter, is poured into the vat, which is well stirred and allowed to settle. The material to be dyed is run through three to five vats, beginning with the weakest, of increasing strength (partially exhausted by

previous dyeings), before passing into the new vat of full strength. Where partially exhausted vats are not available, the following figures will give some idea of the quantities of ingredients to be used in preparing a series of five vats, each of 400 gallons capacity:—

Lbs.	1.	2.	3.	4.	5.
Indigo (60 per cent.),	2	4	8	12	16
Zinc powder,	2	4	6	7	8
Quicklime,	5	10	15	17	20

The vats require sharpening from time to time with small quantities of zinc and lime, in the proportion of 1 to 2. Goods dyed in the zinc-lime vat (as, in fact, with all vats where lime is used) are always acidified, after dyeing, with very dilute sulphuric or hydrochloric acid (about 2 lbs. per 100 gallons of water), and subsequently thoroughly rinsed with water.

Although some vats are more suitable than others for certain classes of goods, the kind of vat chosen for any particular work depends, to a great extent, upon the individual choice of the dyer. For precisely the same kind of work some dyers use the zinc-lime vat, whilst others use the hydrosulphite, prepared either with lime or soda. Much difference of opinion also exists regarding the most suitable size of vat to be used. Cotton is dyed with indigo in all stages of manufacture, but mostly in the form of yarn and piece goods. Yarn is usually dyed by hand in narrow deep vats of about 200 gallons capacity. The hanks are introduced into the vat and moved to and fro under the surface of the liquor, turned two or three times, exposing as little as possible to the air, and, after two to four minutes, taken out and wrung either by hand or by rollers. After allowing the reduced indigo to oxidise, the yarn is taken to another and stronger vat, and the operation repeated until the desired shade is obtained. The white yarn is always entered in the weakest vat, and then dyed in vats of gradually increasing strength. As a rule, vats for this purpose are not fed with fresh indigo, but are gradually worked out, so that each vat in turn becomes the weakest, when, after being exhausted, it is run off and a fresh vat made. Piece goods are dyed either in dipping vats or in continuous dyeing machines. The former vats are used principally for heavy goods and for pieces to be printed by the "resist" process. They are usually rectangular, sometimes round, and have a capacity of 400 to 600 gallons. The cloth is stretched on frames by means of hooks in such a manner that the different folds are kept apart at a distance of about an inch. The frame is then lowered into the vat, where it is allowed to remain for a longer or shorter time (10 to 30 minutes), raised, and the cloth detached and exposed to the air. It is stretched again on the frame and dipped into a stronger vat, the process being repeated until the desired shade is obtained. In some cases the oxidation is accelerated by passing the goods through water between the various dips. For this class of dyeing either the zinc-lime or the copperas vat is usually employed.

The roller or continuous dyeing machine is now very largely used for dyeing cotton cloth, both for plain blue goods and for those to be afterwards printed by the discharge process. A common form of machine (shown in section and plan in Figs. 55 and 56) has two compartments, at the bottom of each of which there is a mechanical stirrer, which enables the sediment to be well stirred up in setting and freshening the vat. The course which the pieces pursue in being dyed is shown in Fig. 55 by means of arrows. They pass from the table on which they are piled at full width over the top of the machine, through the stretching rollers into the first compartment (on the left), thence

into the second, and through the squeezing rollers at the end. From there they pass up and down over the rollers held by the framework fixed above the vat (in order to allow the reduced indigo to oxidise in the fibre), and thence over the top, back through a pair of nipping rollers, and on to the

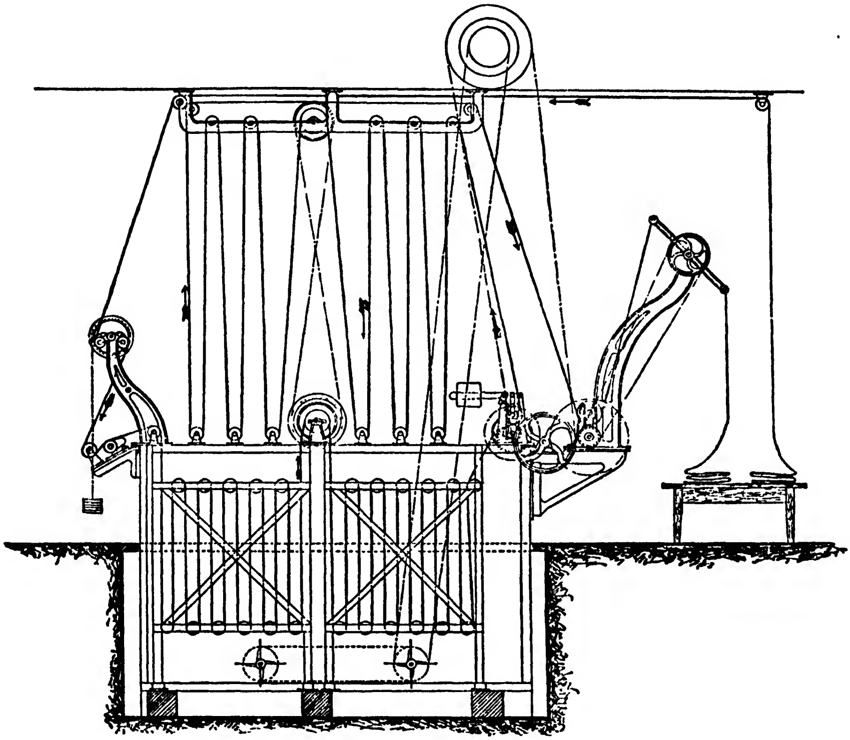


Fig. 55.—Continuous indigo-dyeing machine (section).

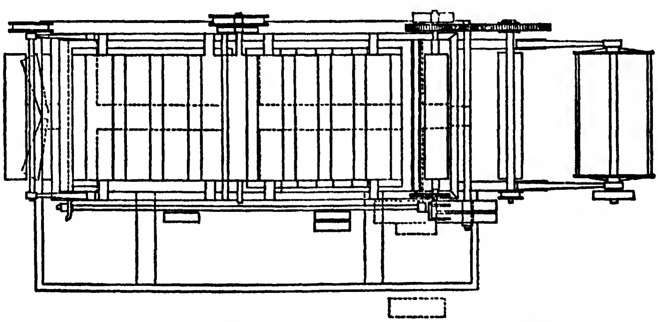


Fig. 56.—Continuous indigo-dyeing machine (plan).

table again. The advantages of this vat over the ordinary ones are that it can be readily cleaned, and the oxidation of the pieces requires very little space. Sometimes four, or as many as six, vats, with oxidising frames between each pair, are worked in a series. Either hydrosulphite or zinc-lime

vats are used. In the former case the oxidising frames must be considerably larger, as oxidation takes place more slowly on account of the excess of hydrosulphite present. Hydrosulphite vats are usually fed from time to time with more indigo, but zinc-lime vats are generally exhausted and made up fresh in turn. A continuous dyeing machine is capable of turning out a great amount of work in a short time, but the goods are not penetrated so well as those dyed in a dipping vat. After dyeing in the hydrosulphite-soda vat the goods are merely rinsed in water, but, whenever lime is used in dyeing, it is necessary to pass them through weak acid (2 to 1,000) before rinsing. A considerable amount of indigo is removed in rinsing, and it is advisable to run the acid bath and first rinsings into settling tanks and recover the indigo by means of some suitable arrangement.

Cold Fermentation Vats.—In Persia, Asia Minor, and other Eastern countries cotton goods are largely dyed in cold fermentation vats. The vessels most frequently used are earthenware jars of a capacity of 50 to 70 gallons. Four to twelve vessels of this kind are often set together in brickwork, and the space between is filled with cattle dung, which, in winter time, is ignited and allowed to smoulder. In this manner the vats are slightly heated, but only to about 20° to 25° C. In summer no external heat is applied, and the temperature is usually from 25° to 30° C. The liquor is never, or very rarely, thrown away. When nearly exhausted a portion of the accumulated sediment is removed, and then fresh indigo and lime are added. The vats are made up much stronger than those used in Europe, and are always strongly alkaline. The quantities vary greatly in different districts, but 6 to 8 lbs. of Bengal indigo are often used for vats of the capacity above mentioned. Synthetic indigo has also been found to be well suited for this kind of vat, and is used in large quantities in the East. In some cases lime (1 to 2 lbs.) is the only other substance added, whilst in others crude potassium carbonate is used as well. Occasionally, if the fermentation is unusually slow, an addition of some saccharine matter, such as raisin syrup or dates, is made, but this is quite an exception. In summer time, under normal conditions, a vat is ready for use in about three days. The material to be dyed, usually cotton cloth in lengths of 5 to 8 yards, is first dipped in a vat which has been already nearly exhausted, then into one of medium strength, and finally into the vat which has been most recently made up. The cloth is pleated in folds and worked from hand to hand under the surface of the liquor, each length remaining three to four minutes in the vat at a time.

The same kind of vat is often used in the East for dyeing worsted yarn, but in this case less indigo is taken, and the material is left in the vat for a much longer time.

Dyeing of Wool.—In England the woad vat and the hydrosulphite vat are the two principal vats employed. In Germany the soda fermentation vat is also largely used. Fermentation vats are employed principally, though by no means exclusively, in the dyeing of heavy cloth, whilst hydrosulphite vats find their chief application in dyeing loose wool, slubbing yarn and lighter fabrics.

Woad Vat.—Fermentation vats, of which the woad vat is a type, require a great amount of skill and practical experience to be worked satisfactorily. Unless the greatest care is taken in conducting the fermentation, much indigo is destroyed. The substances used in the preparation of a woad vat are, besides woad and indigo, bran or sharps, madder, and lime. In fermenting, the starch of the bran is converted into grape sugar, which in turn passes into lactic acid, and then into butyric acid. During the last transformation hydrogen and carbonic acid are formed. The hydrogen in the nascent state reacts upon the indigotin, forming Indigo white. It is important that the

indigo should be in an exceedingly fine state of division, otherwise the reducing action cannot take place, and the particles remain at the bottom of the vat as so much inert matter. The indigo is put into a mill and ground for several days with water until a perfectly smooth paste free from any gritty particles is obtained. The addition of a little caustic soda facilitates the grinding operation.

The vats used for dyeing are either circular or rectangular, and have a capacity of 1,600 to 3,000 gallons. The round vats are generally made of cast iron, and are enclosed in brickwork so arranged as to leave a space for the admission of steam, by which the vats are heated. Rectangular wooden vessels are heated by means of a coil of copper steam pipes arranged inside the vat. In setting a woad vat, so many different ways are adopted by different dyers (all of which lead to good results) that no exact general directions can be given. However, the following description will give an idea of the manner in which a vat is usually prepared in the North of England. Capacity of vat, 2,700 gallons:—

Indigo (60 per cent.),	20 to 40 lbs.
Woad,	5 to 10 cwts.
Bran or sharps,	30 to 40 lbs.
Madder,	10 to 15 lbs.
Lime,	12 to 25 lbs.

[In Germany smaller quantities of indigo and woad are taken, and part of the lime is replaced by soda.]

The vat is filled with water, and heated to 65° C. The crushed woad is introduced, and, after stirring two or three times, left overnight. The stirring is now usually done mechanically by means of a screw fixed near the bottom of the vat, and worked by a movable perpendicular shaft. The next morning the finely-ground indigo, madder, bran, and lime are added, and the whole stirred two or three times during the day, with the addition of 2 to 4 lbs. of lime each time, the temperature being maintained at about 60° C. On the third morning, if the fermentation has proceeded satisfactorily, the vat will exhibit the following characteristics:—The liquid will have a yellowish-green colour, and, on gently stirring it, blue streaks will appear with a coppery scum or "flurry." The sediment will be found to be in an active state of fermentation, and will possess a somewhat sharp, but agreeable odour. If some of the liquor is taken in a ladle and poured back into the vat, the last drops will change slowly from green to blue. The ring of froth formed by pouring the liquor into the vat will remain, and not break up quickly as in the early stages. If the fermentation proceeds too rapidly, it can be checked by the addition of lime. On the other hand, if sluggish, it can be accelerated by the addition of bran. As a rule, a new vat is ready for dyeing in the course of three to five days. The condition of the vat may be ascertained by dyeing a sample of wool for about twenty minutes. On coming out of the liquor the wool should be of a greenish-yellow colour, and should gradually change to green, and then blue. On washing with soap it should only lose a little colour. The temperature of the vat should be maintained at about 50° C. It is not advisable to dye too frequently in a newly set vat.

Before dyeing, the cloth must be thoroughly well scoured, and the soap removed by washing in water. When the vat is ready, and time has been given for the insoluble matters to subside, a 4-inch mesh net (trammel net) or a latticed frame is lowered to a depth of about a yard, so as to prevent the goods coming in contact with the sediment. The ends of the cloth are stitched together in the form of an endless band, and worked under the surface of the liquor by means of a "hawking" machine. This simply consists of a framework supporting a pair of rubber squeezing rollers, which can be lowered

under the surface of the liquid. The older method of working piece goods is to "hawk" them by hand with two iron hooks in full width across the vat backwards and forwards. The goods are kept moving in the vat for various periods of time (usually from half an hour to two hours), according to the shade required, the quality of the cloth, and the condition of the vat. The dye penetrates thick heavy cloth but slowly, and when dark shades are wanted on some classes of goods, the pieces are run for six or eight hours in the vat. They are removed, passed through squeezing rollers, and the colour developed by exposure to the air. In this condition the goods are said to be "grounded," and it is arranged that the shade shall be rather lighter than that ultimately required. They are then passed into a weaker vat, and worked until the desired shade is obtained. Lighter shades are usually dyed direct in one vat. As the goods come out of the indigo vat the colour is a yellowish-green, but on exposure to air it quickly changes to green and blue-green, and finally to the well-known shade of indigo blue. After dyeing, the goods are well washed in water, and cleansed with soap and Fuller's earth in order to remove the indigo which loosely adheres to the outside of the fibres. This operation is of great importance; if imperfectly cleaned, the goods have the objectionable property of "rubbing," which counteracts in a great measure the admirable qualities possessed by indigo. If the pieces, however, had not been thoroughly cleansed before dyeing, or if the vat had been out of condition, no amount of "fulling" would overcome the liability of the goods to rub. Before entering into the indigo vat, piece goods are frequently dyed a light shade of red with barwood, cudbear, or Alizarin red. This "bottoming" with a red colour is necessary with cloth made from shoddy, in order to counteract the grey or brown shade of the material. A deep red "bottom" is often given for the sake of cheapness. It is possible to dye a dark Navy blue with a large amount of red, and a relatively small proportion of indigo.

In the dyeing of loose wool, a strong hempen net or wire basket is used, the material being moved about under the surface of the liquor with poles. Loose wool and slubbing require a greater amount of indigo to produce a given shade than piece goods, each individual fibre being more completely dyed in the interior. Goods which are dyed in the piece only are liable to wear greyish, notably at the seams, the surface of the fibre being rubbed away and the interior dyed a lighter shade, becoming exposed. Goods which have been well dyed in the wool do not show this defect. Sometimes, in order to economise indigo and to produce a cloth possessing a greater resistance to wear and tear, the loose wool or slubbing is dyed a medium shade of blue, and, after being woven, the cloth is milled and dyed up to shade.

During the day's work the vat is stirred once or twice and, if necessary, an addition of lime is made. The want of lime is recognised by the peculiar "mild" smell imparted to a wooden bowl dipped into the liquor, and to the green colour of the solution. Paper prepared with phenolphthalein also forms a good and useful indicator for this purpose. If the paper at once turns clearly pink there is too much lime present. If it comes out of the vat green and develops to a pure blue, a little lime may be added. When the vat is in a good condition, so far as lime is concerned, the drop of liquid running from a strip of phenolphthalein paper dipped into the vat just shows a faint violet tinge. Every evening the vat is well stirred, with additions of ground indigo (5 to 10 lbs.), bran, and lime. It is also warmed up to such a degree that next morning it will have a temperature of about 50° C. When not in use the vats are always kept well covered, so as to retain the heat and prevent oxidation. A vat may be used for a period of from six to nine months, when the liquor clears only slowly and incompletely, and the sediment becomes so bulky that it is difficult to get sufficient clear liquor space for the dyeing opera-

tion. No further addition of indigo is then made, but, as it will still contain a considerable amount of colouring matter, it is used for dyeing light shades, so long as it yields sufficient colour to repay the time. Whenever practicable, it is best to work out an old vat by dyeing loose wool in it. Some dyers convert their old woad vats into hydrosulphite vats, by which means the Indigo is more easily exhausted.

Irregularities of the Woad Vat.—Fermentation vats are liable to get out of order, either from adding too little or too much lime, or from other causes. The most frequent cause is the addition of too much lime, when the vat is said to be oversharpened. Such a state is recognised by a sharp pungent odour, by weakness of the flurry, as well as by the reddening of phenolphthalein paper. The vat dyes wool a greyish shade of blue, and on washing much of the colour is removed. If only moderately oversharp the vat may usually be brought back to a normal condition by allowing it to stand without stirring for a day or so; or several lots of wool intended for dark shades may be successively dyed light shades in the vat. In other cases, the excess of lime is neutralised by very carefully adding hydrochloric acid, sulphuric acid, alum, putrid urine, or stannous chloride. Sometimes a sack of bran, weighted, is introduced into the vat. A vigorous fermentation is thus brought about, and the acid products neutralise the lime. *Mild* vats are recognised by the too sweet smell, by the weak flurry and green colour, and the rapidity by which the drops from a ladle turn blue. This defect is easily remedied by sharpening with lime and stirring well. Under certain conditions a vat "runs away," and much of the indigo is destroyed. Newly set vats, as well as those which are nearly exhausted, are most liable to behave in this manner. It is brought about by a continuous deficiency of lime, which causes a too vigorous fermentation, resulting finally in putrefaction. The blue scum becomes grey, and the bubbles break immediately. The sediment, of a muddy colour, is driven to the surface in lumps. Ammonia and sulphuretted hydrogen are frequently among the products formed. Unless the action has proceeded too far, when all the indigo is lost, the destructive fermentation may be stopped by adding small quantities of lime in rapid succession and keeping the vat well stirred. When the fermentation has become normal it is again fed with indigo, bran, and lime, but much more than ordinary attention is required in its management.

In order to avoid the irregularities to which ordinary fermentation vats are liable, Collin and Benoist* have proposed to employ a completely fermentable food-material and a pure ferment. For a vat of 8,000 litres, 16 kilos. of flour or starch are boiled for a few minutes in water containing 1·6 kilos. of sodium carbonate. The starch paste is transferred to the vat, and 8 kilos. of glucose, 5·38 kilos. of soda, and 1 kilo. of magnesia are added. Magnesia is better adapted for the neutralisation of the lactic, butyric, and other acids formed than lime. With this vat, the amount of alkali necessary to combine with the above-named acids and to dissolve the reduced indigo may be calculated with fair accuracy. As, however, the alkalinity of the vat at the commencement would be too high if the total amount of alkali were to be added at once, there is added upon the first day only one-half of the soda required to neutralise the acids formed in addition to that required to dissolve the indigo. This is calculated to be 230 grms. of soda for 1 kilo. of indigo. Whilst the vat is being worked an addition of 2 kilos. of starch paste and 2 kilos. of glucose will suffice for 100 kilos. of wool per diem. The ferment, *Desmobacterium hydrogeniferum*, is obtained pure by the following cultivation process:—100 grms. of potato cuttings are allowed to digest for some time in 500 c.c. of water at 40° to 44° C. The liquid soon becomes peopled with micro-organisms, among which is the *Desmobacterium*. A flask is now filled with 1·5 grms. of phosphate of soda

* *Journ. Soc. Chem. Ind.*, 1885, p. 493.

3 grms. of tartrate of ammonia, 5 grms. of glucose, 5 grms. of soluble starch, 3 grms. of sodium carbonate, 5 grms. of lime, and 1 litre of water. The flask is provided with a doubly bent tube, which dips into a basin containing 200 c.c. of water. The contents of the flask and basin are boiled for twenty minutes to effect sterilisation, and also to expel air, and then 50 to 60 c.c. of the liquid containing the *Desmobacterium* are introduced into the basin, the boiling being at the same time discontinued. The contents of the basin are slowly sucked into the flask, and when this has cooled down sufficiently for the hand to touch it without inconvenience, the bent tube is dipped under mercury, and the whole maintained for four or five days at a temperature of 38° to 40° C. At the end of this period, the *Desmobacterium* will be in full activity, and in a pure condition; the liquid is then to be absorbed by sawdust sterilised at 150° C., in the proportion of three parts of sawdust to two of liquid. This is dried at 40° to 45° C., and preserved in well-closed bottles. Of this prepared ferment 50 grms. suffice for a vat of 12 cubic metres capacity. It is stated that a saving of 40 per cent. of indigo is thus effected.

The soda or German vat is used extensively on the Continent, but has not found much favour with dyers in England. On the whole, it is more easily managed than the woad vat. It is more suitable for light bright shades; but for dark shades, especially on heavy cloth, the woad vat is to be preferred. The soda vat is prepared with indigo, bran, treacle, madder, sodium carbonate, and lime. Delmart gives the following proportions for a vat of 1,800 gallons capacity:—

Bengal Indigo,	5 lbs.
Treacle,	18 ,,
Madder,	12 ,,
Bran,	60 ,,
Soda crystals,	50 ,,
Lime,	2 ,,

These quantities give a comparatively weak vat. As in the case of woad vats, the proportions of ingredients used by different dyers vary greatly. For a vat of medium strength the Badische Anilin- und Soda-Fabrik recommend the following proportions for synthetic indigo:—

Capacity of vat,	2,000 gallons.
Indigo pure S. (20 per cent.),	40 lbs.
Treacle,	28 ,,
Madder,	10 ,,
Bran,	70 ,,
Soda ash,	40 ,,
Lime,	2 ,,

In place of the 40 lbs. indigo paste 20 per cent., about 13 to 14 lbs. of 60 per cent. Bengal indigo might be taken.

In setting a vat the water is heated to about 65° C. and the above ingredients, irrespective of order, added. The vat is well stirred, covered, and allowed to stand for about 24 hours. It is then examined and treated in a similar manner to the woad vat in its preparation. The vat is fed with indigo, treacle, and lime as required, and occasionally, once or twice a week, about 2 lbs. of soda added. Dyeing is conducted in this vat in the same way as in the woad vat.

Two other fermentation vats may be here mentioned—viz., the potash and the urine vats—though at the present day they are of little importance. The *potash vat* is made up with indigo, madder, bran, potassium carbonate, and lime. It closely resembles the soda vat. The *urine vat* is prepared with indigo, putrid urine, salt, and madder. The indigo white formed during fermentation dissolves in the ammonium carbonate, a constituent of putrid urine.

Hydrosulphite Vats.—These vats may be prepared either with soda or lime, in the same way as hydrosulphite vats for cotton. Two kinds of hydrosulphite-lime vats are recognised—one made with ready-prepared hydrosulphite, which contains but little sediment, and the other where all the ingredients are added to the dye-bath. The latter is the kind of vat which is especially used in England. The reduced indigo is made in separate vessels and added to the dye-bath as required. The solution may be prepared in the same manner as described on p. 315 for *cotton dyeing*, with this difference, that only 12 lbs. of quicklime are taken in place of 24 lbs. Wool requires much less lime than cotton, but more hydrosulphite. The latter may be added in setting the dye-vat. In starting a new vat, the water is run in and heated to about 60° C. For a vat of 2,000 gallons capacity, 4 gallons of bisulphite of soda (52° Tw.), previously mixed with 4 lbs. of zinc powder, are added, and, after stirring, the vat is allowed to stand for at least an hour, preferably longer. The required amount of reduced indigo liquor, according to shade desired, is now added, and the whole well stirred. In about half an hour the insoluble matters will have subsided, and dyeing may be at once commenced.

The liquor should have a greenish-yellow colour, covered with a fine coppery scum. The temperature for dyeing should be about 50° C. For wool, slubbing, and light goods half an hour should be given for each dip. Heavier and tightly woven goods require a longer time for the dye to penetrate. Should the vat become oxidised, indicated by too green a colour being developed, a little bisulphite of soda, previously mixed with one-tenth of its weight of zinc powder, is added. At the same time it will be usually necessary to add a little lime. The proper adjustment of lime requires great care and attention, as either too much or too little makes a great difference in the results. Too much lime is indicated by the liquid having a decided yellow colour and possessing a peculiar slippery feel; also by means of phenolphthalein paper. When in a proper condition for dyeing, this test paper should only show the faintest violet tint, when dipped into the dye-bath.

The *hydrosulphite-soda vat* has found but little application in Great Britain, though it is used to a considerable extent on the Continent. When made up with synthetic indigo, it is quite free from sediment, and with high-class natural indigo, the insoluble matters are trifling in amount. On this account the hydrosulphite-soda vat is peculiarly adapted for use in dyeing machines. When ordinary vats are used, there is also the advantage of smaller vessels being needed, on account of no space being required for a bulky sediment. Naturally, with the employment of caustic soda for wool-dyeing, the greatest care must be taken to avoid an excess.

The Badische Anilin- und Soda-Fabrik recommend the following proportions for a strong vat:—

Capacity of vat, ...	220 gallons.
Indigo pure 20 per cent., ...	10 lbs.
Caustic soda solution (42° Tw.), ...	3 pints.
Hydrosulphite solution (20° Tw.), ...	7½ gallons.

The mixture is heated to about 50° C., and allowed to stand for half to one hour, with occasional stirring. It is then poured into the dye-bath, which has been heated to 50° C., and the whole stirred. After standing for about half an hour dyeing may be commenced. For weaker vats a greater proportion of hydrosulphite is required. For instance, if only 2 lbs. of 20 per cent. indigo paste are taken for dyeing, ⅝ pint of caustic soda lye, 42° Tw., and 3 gallons of hydrosulphite solution, 20° Tw., are recommended. If natural indigo be used, 3⅓ lbs. of 60 per cent. may be taken in place of 10 lbs. indigo pure 20 per cent. A properly prepared bath has a greenish-yellow colour. If yellow, too much

hydrosulphite has been used; if green or bluish-green, too little. The latter can easily be remedied by adding 1 to 3 pints hydrosulphite and stirring. A similar addition of hydrosulphite is required for freshening up after dyeing.

Mention has already been made of hydrosulphite *powder* for use in cotton dyeing. It may also be used in wool dyeing with the same advantages. The Badische Anilin- und Soda-Fabrik recommend the following proportions:—10 lbs. Indigo pure 20 per cent. paste (equivalent to 3⅓ lbs. 60 per cent. Bengal indigo) are mixed with 2 gallons of cold water, 3 lbs. of hydrosulphite powder are added during constant stirring for about ten minutes, when 5 pints of caustic soda, 76° Tw., are added. The mixture is now heated to 60° C. for about an hour, or until complete reduction has taken place. Before adding the reduced indigo to the dye-bath, the latter is heated to 50° to 52° C., and for every 100 gallons of water 1 oz. of hydrosulphite powder is added. For freshening the vat as required about 3 ozs. of the powder per 100 gallons are used. When the vat is being worked continuously it is also recommended to add ammonia two or three times a day in the proportion of half a pint per 100 gallons.

Hydrosulphite powder may also be used for preparing the hydrosulphite-lime vat in the following proportions:—

Indigo (60 per cent.),	20 lbs.
Hydrosulphite powder,	18 ,,
Quicklime,	5 ,,

The indigo is ground to a fine smooth paste, and mixed with about 10 gallons of cold water. The hydrosulphite powder is then slowly added with continuous stirring. This is followed by the quicklime previously slaked and made into a cream. The whole is made up with hot water to 50 gallons, and kept covered (stirring occasionally) for one or two hours at a temperature of 70° to 82° C. The dye-bath is sharpened with hydrosulphite powder as mentioned above, the requisite amount of prepared indigo solution added, and the dyeing proceeded with in exactly the same way as previously described.

Generally speaking, hydrosulphite vats are more easily managed than fermentation vats, and are not so liable to get out of order. A much greater amount of work can be done in a given time, since it is not necessary to wait for a large sediment to subside, as is the case with fermentation vats. When not required the vat can stand for a long time without being spoilt, and in a short time is again made ready for use. As there is very little sediment, the vats seldom need renewal. The goods dyed are cleaner than those dyed in woad vats. There is much less indigo mechanically attached to the outside of the fabrics, consequently there is not so much loss in washing, and there is less liability to rub. The indigo does not penetrate into the interior of heavy and closely woven cloth so well, and for such goods the woad vat is to be preferred. Dark shades are redder and finer dyed in woad vats than in hydrosulphite vats. In hydrosulphite vats, no doubt, a portion at least of the natural red-colouring matter is destroyed or partially converted into indigotin. Under certain conditions—using too much alkali and hydrosulphite—wool is liable to be more or less attacked, acquiring a harsh handle, in the hydrosulphite vat; but the action, by careful management, may be reduced to a minimum.

INDIGO EXTRACT.

It has been previously stated that when indigo is treated with concentrated sulphuric acid, it dissolves, forming mono- and disulphonic acids. According to the subsequent treatment which the solution receives, the

products are known as *chemic*, *acid or sour extract*, *neutral or sweet extract*, *refined extract*, *indigo-carmine*, *soluble indigo*, &c. When a moderate proportion of acid is used and allowed to act for a short time only, indigo-monosulphonic acid is principally formed. This product converted into its sodium salt forms what is known as *red* or *purple indigo extract*. Its use is somewhat limited; the disulphonic acid compounds having a much wider application. For the manufacture of indigo extract, one part of finely-ground dry indigo is slowly mixed with from five to six parts of concentrated sulphuric acid in an earthenware vessel. The best plan is to carefully add the indigo to the sulphuric acid in small portions at a time during constant stirring with a leaden, or, preferably, porcelain stirrer. The vessel is then placed in hot water, at a temperature of 50° to 60° C., for about an hour, taking care to stir the mixture occasionally. It will often be found that after well stirring, dry little balls of powdered indigo rise to the surface. The mixture is allowed to stand covered up for a period of about twenty-four hours. The product thus obtained is known in the dye-house as *chemic* or *Saxony blue*. It was formerly used in this state much more than at present; it now usually receives a further treatment. Unless the indigo is of very fine quality, previous to dissolving in sulphuric acid, it should be broken up into small pieces or ground to a coarse powder and treated with strong hydrochloric acid. After standing about a quarter of an hour, hot water is added, and the whole thrown on to a filter, and the mass thoroughly washed with boiling water. The partially purified indigo is then dried, ground, and dissolved in sulphuric acid as above described. In order to convert the acid solution into "extract," it is diluted with water and treated with a saturated solution of common salt, which precipitates the colouring matter. After standing an hour or two, the mixture is ladled on to a filter, made of strong woollen cloth laid upon wooden frames. Between the cloth and the frame, cocoa-nut matting or straw is placed, in order to allow the liquid portion to run off more freely. By this operation a great portion of the free acid, as well as a valueless green colouring matter, is removed. The pasty mass on the filter is known as *acid indigo extract*. It is left to drain for a period of from one to ten days, according to the "strength" of extract required, and then placed into casks.

Neutral or sweet extract of indigo is obtained in one or two ways. The acid extract may be dissolved in water, reprecipitated by salt and again filtered. In order to remove the free acid completely, the process must be repeated two or three times. The free acid is also removed by neutralising the solution with sodium carbonate, adding salt and filtering as before. A purer extract is obtained (often known as *refined extract*) by filtering the acid solution of indigo, previous to adding sodium carbonate or salt. In this way a considerable amount (varying according to the quality of indigo used) of a dirty green useless colouring matter is removed. The extract may be further purified by dissolving it in water, reprecipitating with salt, and filtering.

A still purer extract is obtained (*best refined extract*) by treating indigotin or refined indigo with sulphuric acid. The refined indigo for this purpose is usually prepared by means of ferrous sulphate and lime. In the first place, what is practically a strong "copperas" vat is made (p. 316). The insoluble matters are allowed to subside and the clear liquid made to travel in shallow troughs a considerable distance, in order to reoxidise the indigotin. The liquid containing indigotin in suspension is then passed through a filter press, and the paste thus obtained dried and ground.

Soluble indigo (*indigo-carmine*) is the best refined extract (neutralised) made from refined indigo, dried and ground. It should dissolve in water without leaving any residue, and should be free from any green impurities.

An exceedingly fine quality of indigo extract may be made from synthetic indigo. The Badische Anilin- und Soda-Fabrik give the following directions for producing it:—1 part of Indigo pure (powder) is slowly stirred into 4 parts of monohydrate sulphuric acid (weak fuming acid), or 8 parts of sulphuric acid, 168° Tw. When fuming acid is used the temperature of the mixture rises considerably, but it should not be allowed to get above 50° C. The mixture is stirred with a thick glass rod and allowed to stand for twelve hours in a warm place. It is then ready for use.

Dyeing.—Indigo extract is not applicable to cotton, but is largely used for silk and wool, although it has been to a considerable extent, replaced by various kinds of Aniline blues. The more acid varieties are employed for dyeing wool, woollen and worsted goods. Neutral extract is employed for silk, and particularly for dyeing the worsted of mixed or union goods. It is also used in printing woollen material and worsted yarn for tapestry carpets, &c. Indigo extract is usually dyed in a bath containing sulphuric acid and sodium sulphate. If the extract is very acid, no further addition is necessary, although within certain limits the more acid the bath is, the better is it exhausted. Sodium sulphate is employed in order to obtain more regular dyeing, the colour working on the wool or silk more slowly. In place of sulphuric acid, alum and tartar are frequently employed.

The shades produced with indigo extract are much brighter than those given by *vat indigo*, but, unfortunately, they are not fast. By conversion into its sulphonic acid derivative, the properties of indigo are entirely changed. Washing with soap and weak alkaline solutions more or less readily removes the colouring matter from the fibre, and, on exposure to light, the shade fades, the time varying of course according to its depth of colour, and the conditions under which it is exposed.

Detection of Indigo and Indigo Extract on the Fibre.—Vat indigo may be found on all fibres, though very seldom on silk. Extract of indigo will not be found on cotton. Indigo being a substantive dye requires no mordant. Consequently, a pure indigo-dyed cloth should contain no mordant. The presence of chromium oxide in the ash of woollen cloth indicates (but does not prove) the presence of logwood or some other mordant dye. Woollen material dyed with *pure* indigo is not affected by hydrochloric acid, dilute sulphuric acid, soap, alkalies, or cold alcohol. Hot soap solutions and alkalies remove some of the colour from cotton dyed with indigo. Boiling alcohol extracts a small quantity of blue colour, but, on cooling, it separates and the liquid becomes colourless. Hot solutions of aniline, amylic alcohol, chloroform, quinoline, ni ro-benzene, glacial acetic acid extract the colouring matter to a greater extent. When the fibre is treated with cold concentrated sulphuric acid, the liquid at first becomes yellow, quickly olive, and slowly changes from green to a deep blue. On the addition of water the solution remains blue; the fibre (if wool) also is usually of a light blue colour. If the solution is boiled with a piece of white wool, the latter is dyed a bright blue shade similar to indigo extract and gives all the reactions of indigo extract. A drop of strong nitric acid gives a yellow spot surrounded by a green ring with indigo-dyed goods. This test is commonly applied by merchants and others to ascertain whether a sample of cloth is dyed with pure indigo or not. The test known as the "nitric acid test" applied alone is of no value whatever, since many other blue colouring matters give practically the same reaction. Some who have discarded the "nitric acid test" apply another, which, however, as a universal test, is also fallacious. They immerse the cloth in hot dilute hydrochloric or sulphuric acid, and if it remains blue conclude that it is indigo. As a test to distinguish between indigo and logwood it is quite satisfactory, but it should be borne in mind that a great number of blue colouring matters resist the action of moderately strong acids remarkably well.

Fabrics (especially cotton goods) dyed with indigo, yield purple-coloured vapours of indigotin when gently ignited. If a piece of porcelain or glass be held over the vapours a blue deposit is obtained. This is not a delicate test, and is of little value when only small quantities of indigo are present on the fibre. In compound shades, indigo, if present, may usually be detected by boiling two or three times with dilute hydrochloric acid, washing with water and then boiling with a weak solution (about ½ per cent.) of sodium carbonate. The fibre is then dried and the various tests above mentioned applied. For the detection of very small quantities of indigo in compound shades (blacks, browns, &c.) a solution of sodium hydrosulphite is a delicate test. The material is boiled with dilute acids, and, if indigo extract is present, afterwards boiled repeatedly with a ½ per cent. solution of sodium carbonate until the whole of it is removed. The fibre is then warmed gently with a solution of the hydrosulphite and the liquid poured into a dish, or filter paper is saturated with it. In a few minutes the hydro-sulphite is oxidised and the reduced indigo (if present) is converted into indigo blues. The blue precipitate may, if necessary, be collected and further treated by heating in a tube to show the purple vapours, &c.

In order to get a deeper as well as a brighter and redder shade on cotton yarn, after dyeing with indigo, the material is often "topped" with Methyl violet or direct cotton reds. Methyl violet is detected by boiling with alcohol, allowing the solution to cool, and filtering. The violet solution may be added to water and a small piece of wool dyed in the liquid. The wool is dried and the presence of Methyl violet confirmed by special tests according to the tables at the end of this work. The presence of direct cotton reds is indicated by white cotton becoming dyed red when boiled in a slightly alkaline solution with the sample of material. The dyed cotton may then be tested with acids, &c., and the results compared with the tables.

Extract of indigo is distinguished from vat indigo by the colour being removed on boiling with a dilute solution (½ per cent.) of sodium carbonate. On the addition of an acid to the solution, the colour is intensified, and wool or silk may be dyed blue in it. The acidulated solution is decolourised by potassium permanganate. Strong hydrochloric acid turns the fibre greenish-blue and caustic soda green. Nitric acid gives a yellow spot as with vat indigo.

In the *Journal of the Soc. of Dyers and Col.*, 1887, pp. 127, 140, 159, 178, a series of tables are given by W. Lenz, for detecting various other colours in indigo-dyed goods.

Estimation of Indigo on the Fibre.—Various methods have been proposed for the *estimation* of indigo in dyed material. For wool and woollen fabrics (in the absence of other colouring matters) fairly good results may be obtained by simply treating with concentrated sulphuric acid, filtering through glass wool, and washing at first with pure sulphuric acid, and finally with water. The solution is made up to a known bulk, and the amount of indigotin present determined colorimetrically. The method is not suitable for cotton goods or mixed fabrics. Indigotin on cotton may be conveniently estimated by means of sodium hydrosulphite and lime, as described under analysis of indigo. In this case the regenerated indigotin should be collected on an asbestos filter, washed, dried, dissolved in concentrated sulphuric acid, and the indigotin determined either colorimetrically or by permanganate. Indigo on dyed material may also be estimated by means of the various volatile solvents described under analysis of indigo. Gerland recommends the use of nitrobenzene for this purpose, and finds that the extraction takes place much more rapidly if the material is treated in the first place with boiling acetic acid. He prefers, however, to destroy the fibre (wool or cotton) with strong mineral acids before extracting with nitro-benzene. Brylinski recommends the use of acetic acid for extracting indigotin from the fibre (see *Analysis of Indigo*). Binz and

Rung* also use glacial acetic acid in determining the proportion of indigo fixed on the fibre in dyeing.

From 5 to 10 grms. of the dyed material are placed in a Soxhlet's apparatus and extracted with about 100 c.c. of glacial acetic acid. The extraction should be completed without interruption. According to depth of shade and texture of material from two to ten hours are required to completely extract the colour. On account of the liability of other substances being extracted (especially from cotton), instead of attempting to weigh the indigotin as usually recommended, it is best to collect it on asbestos, wash well with hot water, dry, dissolve in concentrated sulphuric acid, and titrate with potassium permanganate, sodium hydrosulphite, or titanous chloride.

LOGWOOD.

Logwood is one of the most important of all dyestuffs. It is usually classed as a red-wood, although it is used principally for the production of blue and black shades.

The colouring principle itself is of a distinct red colour, but in combination with the more important mordants, it gives blue, violet, and black lakes.

Logwood, or Campeachy wood, is the product of a large tree of the leguminous family, known botanically as *Hæmatoxylon campechianum*, which grows abundantly in the West Indies, Mexico, and several States of South America. The best commercial qualities are obtained from Honduras, St. Domingo, and Jamaica. The finest wood was formerly imported from Campeachy, but the supply is now almost exhausted.

Logwood was introduced into Europe by the Spaniards shortly after the discovery of America. It does not appear to have been used in England as a dyestuff until the time of Elizabeth, and then its use was only of short duration, since by an Act of Parliament it was forbidden to be used for dyeing under severe penalties on the ground that it produced fugitive colours. Large quantities of logwood were burned, and indigo suffered in a similar manner. This law was enforced for upwards of a century, but was repealed during the reign of Charles II., by which time better methods of application had been discovered.

In Germany Frederick the Great issued an edict in 1758 forbidding the use of logwood for the dyeing of white cloth, while in France, under Colbert's administration, logwood was officially classed as a loose colour.

Logwood is imported in the shape of irregular blocks or logs. When the trees are freshly felled the wood is colourless, or nearly so. By the time the logs arrive in Europe the outside is of a dark brownish-red colour, while the interior is only pale yellow or light orange.

The colouring principle of logwood was first investigated by Chevreul in 1810. Erdmann, in 1842, examined it further, and named the compound *hæmatoxylin*. This body on oxidation yields *hæmatein*, which is the real colouring matter in prepared logwood.

Hæmatoxylin is the result of the decomposition of a glucoside which exists in the fresh wood. Regarding the glucoside itself, little is known, except that under the influence of a species of fermentation it is decomposed with the formation of sugar and hæmatoxylin. W. M. Gardner † considers that during the "ageing" of logwood little or no fermentation takes place, and that the process is merely one of oxidation; the hæmatoxylin assumed to exist in the freshly-cut wood being slowly converted by the oxygen of the air into hæmatein. The same view is upheld by Hummel.‡

* *Zeit. angew. Chemie.*, 1898, p. 904; *Journ. Soc. Dyers and Col.*, 1899, p. 74.
† *The Dyer and Calico Printer*, 1891, p. 8.
‡ Thorpe's *Dict. of Applied Chemistry*, II., p. 473.

Hæmatoxylin, $C_{16}H_{14}O_6 + 3H_2O$, when perfectly pure, forms white prismatic crystals, but, as already stated, they quickly become coloured on exposure to the air, especially when moist, with the formation of hæmatein. Hæmatoxylin may be obtained by treating the finely-powdered wood or the extract of logwood with ether, evaporating the ethereal solution to a syrup, adding a little water, and allowing it to stand for some days, when hæmatoxylin crystallises out. It is only sparingly soluble in cold water, more readily soluble in hot water, and freely soluble in ether, alcohol, and carbon bisulphide. It is non-volatile, and on being heated is decomposed. On fusing with caustic potash, pyrogallic acid is formed, which shows an intimate relation between the colouring matter of logwood and the compounds of the benzene series.

Hæmatoxylin acts as a weak acid, combining with bases to form salts which rapidly absorb oxygen from the air, being thereby converted into hæmatates. Alkali dissolves it with a reddish-purple colour, which quickly becomes brown in the air.

Hæmatein, $C_{16}H_{12}O_6$, is produced from hæmatoxylin by the abstraction of two atoms of hydrogen, a change which takes place by the action of oxygen, especially in the presence of alkalies—

$$C_{16}H_{14}O_6 + O = C_{16}H_{12}O_6 + H_2O.$$

It constitutes the crystallised constituent of the "Hæmatine" of the West Indies Chemical Co., and can be readily separated from the other substances by repeated extraction with hot distilled water. Like hæmatoxylin, hæmatein is only slightly soluble in cold water, but more soluble in hot. Its solution is decolourised by sulphuretted hydrogen, although it is not reconverted into hæmatoxylin. It combines with alkalies, forming definite salts, hæmatates, which are freely soluble in water. On exposure to air, further oxidation takes place with the formation of brown insoluble bodies.

Ageing or Maturing of Logwood.—In order to bring about the decomposition of the glucoside, and the conversion of the hæmatoxylin into the colouring matter proper—hæmatein—the wood is either rasped or chipped, and after the addition of a certain amount of water (about 25 per cent.), placed in heaps of about 20 feet long, 10 to 12 feet broad, and 3 or 4 feet high. The heaps are frequently turned over in order to allow the air to act upon the hæmatoxylin, and also to prevent a too great elevation of temperature, which would cause excessive fermentation, resulting in the complete destruction of the colouring matter. This operation, the so-called *ageing* or *maturing* of logwood, simple as it may appear, requires the greatest care and skill in its management. The state of the atmosphere has a great effect upon this process of fermentation. On a warm, dull and foggy day the whole of the colouring matter in hundreds of tons of wood may be destroyed in the course of a few hours. At such periods the heaps of chipped or rasped wood in process require constant attention, otherwise excessive oxidation ensues, with the results already mentioned. When this has occurred the wood is said to be "overheated," "burnt," or "killed." Its colouring matter is not worth extracting, and if the "heating" once sets in it cannot be checked, and the whole lot is practically rendered worthless. The nature of this change is not known. It may possibly be due to the development of some micro-organism, which, in some way or other, destroys the colouring matter, in a similar manner to the destruction of indigo by excessive fermentation in a woad vat.

When the fermentation of the wood proceeds in a satisfactory manner, the hæmatoxylin is more or less completely converted into hæmatein by the oxygen of the air. The ammonia formed by decomposition of the nitrogenous matters present no doubt plays an important part in the production of the colour. In order to accelerate the operation the wood is sometimes watered

with a solution of glue—a highly nitrogenous body—but the practice is attended with considerable risk of spoiling the colouring matter. Prepared or matured logwood contains from 20 to 30 per cent. more water than the original wood. During the process of "ageing," the colour of the wood changes from a yellowish-brown to a rich red-brown or dark crimson.

A decoction of matured logwood contains both hæmatoxylin and hæmatein, since the former is rarely entirely converted into hæmatein during the process of fermentation. The best logwood yields only about 3 per cent. of its weight to boiling water, and not more than 1 per cent. to cold water. A decoction of logwood, according to its strength, possesses an orange-yellow to a dark rich reddish-brown colour. It gives strikingly characteristic reactions with acids, bases, and various metallic salts.

Weak acids turn the solution paler.

Concentrated acids give a blood-red colouration, which becomes orange-yellow on dilution.

Potash and soda give at first a purple colour, which becomes quickly blue, and more slowly dirty violet or brown.

Carbonates of the alkalies give similar reactions, but the colour is redder, and does not become violet.

Ammonia gives a deep reddish-purple, which very quickly turns brown.

Baryta and lime water produce dark violet—nearly black—precipitates.

A solution of alum gives a beautiful rich plum colour, which develops slowly.

Normal acetate of lead gives a very dark violet precipitate.

Basic acetate of lead—bluish-black dark indigo-blue precipitate.

Ferrous sulphate—violet-black precipitate.

Ferric sulphate—similar, but redder.

Copper sulphate—dark red precipitate, which quickly becomes violet.

Stannous chloride—rich reddish-violet precipitate.

Nitrate of silver—yellowish-brown precipitate.

Bichromate of potash gives a black colouration, which develops slowly; on boiling a black precipitate is produced.

It should be observed that the colours produced in many of these reactions vary somewhat, according to the strength of the logwood decoction. In a very dilute solution, for example, lime water, instead of giving a dark violet precipitate, produces a reddish-purple colouration.

Dyeing.—Logwood is used by the dyer in various forms, according to the class of goods to be dyed, and the shade to be obtained—

1. The wood in the form of chips or raspings.
2. Logwood liquor—a decoction of the wood.
3. Logwood extract, in the form of paste or solid, obtained by evaporating the decoction.

Logwood is very extensively employed in the dyeing of all textile fibres and all classes of fabrics. Immense quantities are used for dyeing wool, cotton, and silk black, for which purpose, as a rule, the dyer prefers the chips or raspings, both on the ground of being more economical, and giving a tone superior to the extracts. In cotton dyeing extract is principally used. In the dyeing of loose wool, slubbing, or yarn, the usual practice is to weigh out the requisite amount of *chipped* wood into hempen bags, and suspend them in the dye-vessel by means of sticks laid across, and boil for twenty minutes or half an hour. The bags are then taken out, allowed to drain, and after adding a little cold water to the vat to reduce the temperature, the material to be dyed is entered. The wood which has been thus treated is extracted a second or sometimes a third time. If, for example, it is found desirable to use 80 lbs. of wood for a certain amount of material, this might be divided into four bags, and, at the same time as these bags of wood are being boiled in the vat, four more are immersed which have been once extracted, and four others

which have been twice extracted. After these extractions the wood is found to contain very little colouring matter, and may be taken away and burnt. The woollen and worsted piece dyer uses, as a rule, rasped wood, since the fine particles are more easily removed in washing than chips. It is preferable, however, to make a decoction of the wood in a separate vessel designed for that purpose, and run the clear liquid only into the dye-vat. This is now done in many dye-houses. It should be remembered, however, that a *weak* decoction of logwood deteriorates on keeping.

Logwood Extract.—In the dyeing of cotton and other vegetable fibres, as well as in printing, and latterly also to some extent in wool dyeing, logwood is used by preference in the form of extract. Such extracts are obtained by extracting the chipped unaged wood in a series of wooden or iron vessels, which are worked on the counter-current principle. The extraction is either effected on the French system without pressure, when a smaller yield, but better quality, of extract results; or on the American system under pressure, which results in a larger yield, but inferior quality. The liquors thus obtained are evaporated down in vacuum pans to the standard strength of extracts in general use (51° Tw.), or they may be evaporated down to such a consistency that they solidify on cooling.

Ordinary logwood extracts are from three to four times as strong as the "aged" wood, but whereas the latter contains principally hæmatein, the former contain principally the unoxidised hæmatoxylin, which occasionally separates out in crystals. Cheap logwood extracts, especially such as are used for black dyeing, frequently contain chestnut extract, while Glaubersalt, molasses, and other substances are sometimes added in order to increase the specific gravity. According to a recent patent of Lepetit, Dollfus & Gansser,* the addition of magnesium sulphate (15 to 20 per cent. of the weight of the logwood) to the extract has the effect of producing a much deeper black in dyeing.

Within recent years oxidised logwood extracts have been placed on the market, in which the hæmatoxylin has been either partially or wholly converted into hæmatein by artificial means. This may be effected, according to H. P. Wells (German Patent No. 76,507), by heating to 60° with the addition of a small amount of nitrite of soda, or, according to Matheson (U.S.A. Patent No. 542,403), by precipitating the colouring matter by the addition of borax, when oxidation takes place presumably by air contact. By evaporating the logwood liquor down with the addition of ammonium carbonate, a similar oxidation is effected, but it is doubted by some whether such artificially-prepared extracts yield such fast colours as ordinary extracts in the matured wood.† Under the designation "Alligator Brand," the West Indies Chemical Co., of Jamaica, has for some years brought logwood extracts into the market which are manufactured where the wood grows. These extracts are supplied in any degree of oxidation from an extract containing 95 per cent. of the colouring matter as hæmatoxylin to one containing hæmatein only. The choice of the extract will naturally depend on the use to which it is to be put, but principally on the nature of the mordant—*i.e.*, whether it is an oxidising agent or not.

Extracts of logwood find their chief application in cotton dyeing, but are also used on wool for the dyeing of blues and compound shades, such as greens, olives, drabs, and browns, when, comparatively speaking, only small quantities of colouring matter are required.

Logwood is an adjective dye, and can therefore only be applied to the textile fibres through the medium of a mordant.

* English Patent No. 9,604, 1905; see also *Journ. Soc. Dyers and Col.*, 1905, p. 251.

† See *Journ. Soc. Dyers and Col.*, 1895, pp. 125 and 181.

The mordant may be applied in various ways—(1) before the dyeing operation; (2) afterwards; (3) the dye and mordant may be applied together in the same bath; (4) the material may be mordanted first, then dyed, and again passed into a mordant bath. The last operation is termed "saddening" or "finishing," and when the mordant is a *bichromate* the process is sometimes named "back chroming."

Logwood with the more important mordants gives the following shades:—

Bichromate of potash, ...	Blue to black.
Salts of alumina, ...	Greyish violets.
,, iron, ...	Grey to black.
,, copper, ...	Dull greenish-blue.
,, tin, ...	Bright reddish-violet.

Dyeing of Cotton.—Logwood is most usually applied to cotton for blacks, greys, &c., through the medium of iron mordants, such as acetate or pyrolignite of iron, "nitrate of iron" (ferric sulphate), and ferrous sulphate (see p. 266). The iron oxide may be fixed direct or by means of a tannin, such as sumach or myrabolans (see p. 186). The better black is obtained by tannin. For this purpose the cotton cloth or yarn, after being thoroughly wetted out, is steeped overnight in an infusion of myrabolans (about 40 per cent.); the excess of liquor is then removed by squeezing (not washing), and the cotton passed through a weak solution of lime, which causes a tannate of lime to be formed on the fibre. The material is then worked in a bath containing acetate or "nitrate" of iron or copperas at about 4° Tw. for about half an hour, again passed through weak lime water, and well washed. The tannate of iron thus formed on the fibre imparts to the cloth or yarn a deep grey colour, and, consequently, less logwood is required to produce a black than when the material is mordanted with iron salts only. Pieces are generally prepared by running through a stronger solution of tannin material in a machine known as a "jigger." The cloth or yarn is dyed in a separate bath with 30 to 50 per cent. of logwood, and, if necessary, a small amount of fustic and usually a little copper sulphate. The dyeing is commenced cold, and the temperature of the bath slowly raised to the boiling point. In order to obtain a cleaner and faster black the cotton, after dyeing, is passed through a hot weak bath of potassium bichromate or "nitrate of iron;" and, after washing in water, scoured in soap, which takes away any rusty appearance, and thereby gives a more agreeable tone.

The following is an example of dyeing a *black* on cotton yarn. The quantities are for 60 lbs. yarn:—

1. Enter in a hot solution of sumach extract (6 quarts extract (53° Tw.) in 120 gallons of water). Give three turns and allow to steep overnight.
2. Sadden in a solution of "nitrate of iron." For the first lot of yarn take 2½ gallons of "nitrate of iron" (80° Tw.) to 180 gallons of water. For subsequent lots add ¾ gallon to the same bath.
3. Pass through lime water or a bath containing 4 lbs. of suspended chalk.
4. Dye in a bath containing logwood and fustic, using 5 lbs. of solid logwood extract and 1 lb. of fustic extract of 53° Tw.
5. Sadden in dye-bath with 1 lb. of copperas.
6. Soap at 140° F. with 4 lbs. neutral soap.

Practically the same process may be used for pieces, the first operation of steeping being replaced by slop-padding in the sumach extract and then drying over tins.

In the dyeing of cotton warps, and also largely in the case of piece-goods, a continuous process is employed, the goods passing in succession through the various baths.

A common method used in piece dyeing is to pad in pyrolignite, dry, pass through lime water, and dye up in logwood. Another method largely used for all cotton and cotton warp fabrics (linings, &c.) is to prepare with tannin. pass through copper sulphate, and dye in logwood.

The following method is taken from the patent specification of Lepetit, Dollfus & Gansser (English Pat. No. 9,604, 1905):—A short bath is prepared with pure dry logwood extract (5 per cent.) and 15 to 30 per cent. magnesium sulphate (on the weight of the extract). The cotton is turned for an hour at the boil and is then left in overnight. Next morning it is wrung, steeped for half an hour in a cold bath containing 2½ per cent. copper sulphate, rinsed, wrung, and returned to the hot logwood bath for an hour. It is then wrung, treated as before with copper sulphate, again immersed for an hour with the addition of 1 per cent. ammonia soda, wrung, and steeped for half an hour in a cold solution of copperas. Finally, dyeing is again effected with the addition of 1 per cent. soap.

There are various methods of obtaining chrome blacks on cotton, but they are not very largely used. Perhaps the fastest is that obtained by three baths. The first bath contains a strong decoction of logwood, equal to about 500 lbs. of logwood for 100 lbs. of cotton. Of course the bath is kept for subsequent lots a much smaller quantity being required afterwards. The cotton is boiled in this bath for about an hour, taken out and exposed to the air for some time and then worked in a cold solution of 6 to 8 per cent. of potassium bichromate and 5 per cent. of copper sulphate for three-quarters to one and a half hours. The cotton is washed and again entered into a logwood bath containing about 100 per cent. of logwood. In this bath the cotton is introduced cold and the liquid gradually raised to the boiling point. Chrome blacks on cotton may be produced in one bath either by means of chromium acetate or by a mixture of potassium bichromate and hydrochloric acid. The dye liquors must be very strong.

A logwood black may be also dyed on cotton in one bath by the aid of copper mordants. Copper acetate and copper carbonate are the salts usually employed. The copper carbonate is produced in the dye-bath itself by mixing sulphate of copper and soda ash in proper proportions.

A purple may be obtained on cotton with logwood by mordanting with stannous chloride. After immersing the material in a weak bath of stannous chloride, the cotton is washed in water which causes a precipitate of oxychloride of tin to form on the cloth. It is then dyed in a fresh bath of logwood decoction, entering cold, and gradually raising the temperature to the boiling point.

A logwood blue is dyed either in a single bath or two baths by means of copper acetate or sulphate. The shade closely resembles the blue obtained by indigo, but it is not fast to light.

Direct black on cotton piece goods. (Noir réduit.)

100 litres (10 galls.) logwood extract (53° Tw.)
10 kilos. (10 lbs.) bichromate of potash.
50 litres (5 galls.) acetic acid.

Dissolve the bichromate in the acetic acid and add this solution to the logwood extract, stirring for one hour. Add

25 kilos. (25 lbs.) chrome alum.
1¼ ,, (1¼ lbs.) oxalic acid.
12½ litres (1¼ galls.) bisulphite of soda at 64° Tw.
25 ,, (2½ galls.) pyrolignite of iron at 15° Tw.

Stir for four hours at 75° C.

Colour.

16 kilos. (16 lbs.) starch.
55 litres (5½ galls.) water.
40 ,, (4 galls.) direct black.
15 ,, (1½ galls.) acetic acid.
10 ,, (1 gall.) tragacanth thickening.
1¼ ,, (1 pint) oil.
2½ ,, (2 pints) Persian berries extract (53° Tw.)

Boil up and allow to cool.

Add 5 litres (½ gall.) acetate of chrome (32° Tw.)
2½ ,, (2 pints) bisulphite of soda.
2½ ,, (2 pints) turkey-red oil.

Pad the pieces in a printing or padding machine, steam, chrome lightly, and soap (*H. Koechlin*).

Dyeing of Wool.—As already stated large quantities of logwood are used for dyeing wool black. Blacks are produced either by chromium mordants or iron mordants, and are distinguished as "chrome" blacks and "iron," or more usually as "copperas" blacks.

Copperas black is the oldest of the logwood blacks, and formerly was used much more than at the present time. It has been to a great extent superseded by the introduction of bichromate of potash as a mordant. A copperas black, however, if well dyed, is superior in many ways to a "chrome" black. It is less liable to turn green on exposure to light, and it is also stated that cloth dyed with "copperas" possesses a "kinder" and softer handle than cloth dyed with chrome. A copperas black may be obtained either by mordanting before dyeing or mordanting afterwards. The latter is the more usual custom. The material is boiled for one to one and a half hours with a decoction of logwood and usually a little fustic; the amount of each varying according to the quality of the wool, texture of the fabric, and the shade desired. The quantities required may be between 40 and 100 per cent. of logwood and 5 to 12 per cent of fustic, calculated on the weight of the material to be dyed. After dyeing, the mordanting or "saddening" may take place either in the same bath or in a separate vessel, the latter being preferred. For this operation about 5 per cent. of ferrous sulphate (copperas) and 1 to 2 per cent. of copper sulphate (blue vitriol) or copper acetate (verdigris) are added to the bath, the wool is re-entered, and boiled for from three-quarters to one hour. The addition of a copper salt makes the black faster to light, and it is also considered that it assists in developing a fuller black by virtue of its oxidising action upon the hæmatoxylin. The wool must not be washed between the operation of dyeing and saddening, otherwise much colouring matter will be lost, since it is not yet fixed in the fibre but merely absorbed by it.

When the wool is mordanted previously to dyeing an addition of bitartrate of potash, in the form of tartar or argol, is made to the mordant bath, in order to prevent the unequal precipitation of oxide of iron on the fibre. Alum and copper sulphates are usually added as well as "copperas." The wool is mordanted at or near the boiling point for one and a half hours with 5 per cent. ferrous sulphate, 1 to 2 per cent. of copper sulphate, 1 to 2 per cent. of alum, and about 10 per cent. of tartar or argol. It is taken out, squeezed, and allowed to lie in a heap for some hours, usually overnight, before dyeing. The dyeing is then proceeded with in a fresh bath, with 40 to 80 per cent. of logwood, and a little fustic, for one and a half hours at the boiling temperature. The addition of a little calcium acetate to the dye-bath increases the intensity of colour. This addition is, however, unnecessary and superfluous in the case of waters containing a moderate amount of lime salts. Although decidedly beneficial,

it is not clearly and definitely known what action takes place when the wool is allowed to lie for some time after mordanting. The simplest view to take is that the ferrous oxide in the fibre is partially oxidised to ferric oxide. Numerous modifications of these processes are adopted in particular cases. For instance, small proportions of madder, cudbear, orchil, sumach, &c., are added to the dye-bath in order to produce fuller and faster blacks.

A copperas black may be produced in a single bath on wool, but great care must be taken to have the necessary ingredients in proper proportions. A well-known black of this description is *Bonsor's patent fast direct black*, which is sent out in the form of a paste. It consists of the colouring matter of logwood in combination with oxides of iron and copper. Only small quantities of copper salts are present. The substance is insoluble in water, but is readily brought into solution by means of oxalic acid, which changes the bluish-black liquid to amber-brown. For 100 lbs. of wool about 40 lbs. of paste are required for the first bath. After the paste has been thoroughly mixed with the liquor, 3 to 4 lbs. of oxalic acid are gradually added until the solution becomes of a dark amber-brown colour. The exact amount of oxalic acid to be added can only be determined by practice. If the bath is too acid the colour produced is thin and takes a long time to develop; but, on the other hand, if not sufficiently acid, the colour is not fast although it develops more quickly. The dyeing usually requires from one and a half to two and a half hours, at or near the boiling point; after some time a little sodium carbonate might be advantageously added in order to neutralise the acidity which increases as the dyeing proceeds. The black paste itself produces a blue black, but, if a dead black is required, all that is necessary is to add some yellow colouring matter, such as fustic. As the bath is acid, one may also use some of the many acid coal-tar colours —red, yellow, or blue—to modify the shade as required. The bath used for dyeing the direct black is kept, since much of the colouring matter is left in solution and a smaller quantity of the black paste is required for the subsequent lots to be dyed. Oxalic acid is again added as required. A black, properly dyed in this manner, stands the action of light well.

Chrome Blacks.—Although bichromate of potash has been known as a mordant for logwood, &c., for some sixty years, many dyers have still much to learn regarding its proper use. It is most important that not more than a certain amount of potassium bichromate should be used, and the effect of substances added to the mordanting bath should be carefully taken into consideration. If too much bichromate is used, the colouring matter is gradually destroyed and the dyed fabric acquires a green shade.* Chrome blacks are almost invariably obtained by first mordanting and then dyeing. In mordanting, about 3 lbs. of potassium bichromate are usually taken for 100 lbs. of wool, and the material boiled for three-quarters to one and a half hours. For the first bath rather more potassium bichromate is required. It is not necessary that the liquor should be actually in ebullition, but it should be very near the boiling point. There is a very considerable difference in mordanting, say at 80° C. and at 95° C. After mordanting, the wool must be well washed, as it is important that all excess of potassium bichromate be removed. With slubbing and yarn the washing is done by means of a shower. Piece goods are washed in a machine designed for that purpose. The material is then dyed in a fresh bath for one to one and a half hours, at the boiling temperature, with 50 to 80 per cent. of logwood and 5 to 10 per cent. of fustic. The fastness of the black to light is much increased by adding some red or violet colouring matter to the dye-bath. The substances used for this purpose are Alizarin red, Gallein, Gallocyanin, cudbear, orchil, camwood, &c. The best colouring matter to use is undoubtedly Alizarin red, as it is much faster than any of the other reds and works well with

* J. B. Wilkinson, *Journ. Soc. of Dyers and Col.*, 1886, p. 36.

logwood. The bath should not be at a higher temperature than 80° C. when the wool is entered. Cudbear and orchil are often used, but the colouring matter is not fast to light. Gallocyanin, sold under the names of Alizarin violet, Alizarin purple, New fast violet, &c., is very good, and gives the black a rich bloomy appearance. Camwood, barwood, &c., are sometimes applied to the wool before chroming for the same purpose. Common blue-blacks and dark navy blues are frequently dyed after chroming in a bath containing logwood, sulphuric acid, Glauber-salt, and Soluble blue or extract of indigo. The colour, however, on exposure to light soon loses its bloom, becoming grey. Blacks which have to be clean to washing require another bath after dyeing. When goods are taken from the dye-bath they always contain some excess of colouring matter which is simply absorbed by the wool. The object of the third bath is to precipitate and fix this colouring matter in the fibre. The substance usually employed is potassium bichromate, but much less should be used than in mordanting. In this finishing or back-chroming bath the temperature of the liquor should not be higher than about 80° C., and the amount of potassium bichromate used should not exceed 1 per cent. of the weight of the wool. It is often in this finishing bath that by the use of too much potassium bichromate the black is rendered liable to turn green on exposure to air. A dyer of slubbing or yarn is frequently required to dye the material submitted to him so that it will not discolour boiling distilled water. The consequence is in many cases he uses too much potassium bichromate in the finishing bath, obtains clean black, but one which will probably turn green on exposure to light. Rawson* has examined a great number of samples of black wool which have turned green on exposure, and in every case an excess of chromium was found.

It is difficult to state a maximum amount of chrome which should be present on the fibre, since much depends upon its condition—*i.e.*, whether present as chromium oxide or as a chromate. The chromate is decidedly the more injurious. Now, when an excess of potassium bichromate is used in "back chroming" or finishing a great portion of it undoubtedly remains on the material as chromate. If too much has been used in the first chroming any chromate fixed on the fibre is, no doubt, reduced to chromic oxide at the expense of the colouring matter of the logwood. To give an approximate idea of the amount of chromium which should be present, the following case may be cited:—Of two samples of yarn dyed by the same dyer under practically the same conditions, one was found to turn green in a very short time, whereas the other remained unchanged. It was found that the one which turned green contained chromium equal to 1·62 per cent. of potassium bichromate, and the other equal to 1·1 per cent.

Instead of using potassium bichromate in the third bath, one may use other salts, which, however, are generally added to the dye-bath when the dyeing has been completed. If 3 per cent. ferrous sulphate is added, and the goods worked for about a quarter of an hour longer, a dead black is obtained, and the excess of colouring matter is at the same time fixed, although the material is not as *clean* as if it had been finished with potassium bichromate. If 2 per cent. of stannous chloride is added in place of the ferrous sulphate a rich violet-black is produced. The same effect is obtained by using Gallocyanin with the logwood.

In mordanting with potassium bichromate, frequently other substances, such as acids or acid salts, are added to the bath. Sulphuric acid is the most common addition; but it should never exceed one-third the amount of potassium bichromate, otherwise the shade obtained with logwood is dull. When the proportion of acid employed is as 1 to 3 of bichromate the solution practically

* *Journ. Soc. of Dyers and Col.*, 1889, p. 188.

contains chromic acid and sulphate of potash, as shown in the following equation :—

$$K_2Cr_2O_7 + H_2SO_4 = 2CrO_3 + K_2SO_4 + H_2O.$$
$$\text{(295 parts.)} \quad \text{(98 parts.)}$$

Under these conditions, a greater amount of chromium is fixed on the fibre than when potassium bichromate alone is used, but the wool is considered by many dyers to be slightly injured, chromic acid being a very powerful oxidising agent. The addition of organic acid and organic acid salts to the "chrome" bath is decidedly advantageous, the substances usually employed being tartar (bitartrate of potash), tartaric and oxalic acids. The immediate effect of these substances is to produce the deposition of green chromic oxide in the fibre instead of chromic acid. Wool mordanted with potassium bichromate alone, or in conjunction with sulphuric acid, is of a dull yellow colour, but when organic acids are used it becomes of a pale green colour. When 3 per cent. potassium bichromate is used, from 4 to 5 per cent. of oxalic acid or tartaric acid or 8 per cent. of tartar is required to give the best results. It would be more economical to use 5 per cent. of tartar, with addition of 1 per cent. of sulphuric acid. Such large quantities of organic salts, however, are rarely used in practice on account of the expense. In place of tartar or oxalic acid, lactic acid is now largely used, likewise formic acid and "lignorosine."

The shades obtained with logwood on wool mordanted with chromic oxide are both brighter and faster than those in which the mordant was chromic acid. Probably the principal reason that tartar and tartaric acid have not been universally adopted in chroming is the expense. It has been shown, however, that the same effect can be produced in a much cheaper way, and with superior results. The wool is mordanted as usual with potassium bichromate, with or without the addition of sulphuric acid. It is then immersed for a few minutes in a bath containing bisulphite of soda (5 per cent. on the weight of the wool), which quickly changes the yellow fibre to green. After washing, the wool is dyed as usual.

Since the chromium in chrome alum already exists in the form of chromic oxide, one might naturally expect chrome alum to give better results than potassium bichromate, but this is not the case. The colour obtained is not uniform and regular, and in order to obtain a full shade a very large amount of tartar must be used.

In the usual method of mordanting with potassium bichromate alone there is, in most cases, a considerable waste of this mordant. In an old chrome bath there is a gradual accumulation of chromate which might with advantage be utilised.* A dyer usually adds—and, for reasons about to be explained, is obliged to add—more potassium bichromate than is taken up and removed by the wool. This is due to the fact that when wool is boiled with potassium bichromate the latter is partially decomposed, chromic acid or a chromate (as well as chromic oxide) being fixed by the fibre and neutral potassium chromate remaining in the bath. If the material has been previously scoured it takes alkali into the bath which at once neutralises the potassium bichromate to potassium chromate, as shown in the following equation :—

$$K_2Cr_2O_7 + Na_2CO_3 = K_2CrO_4 + Na_2CrO_4 + CO_2.$$

The normal chromate is a much less active mordant than potassium bichromate, in fact one may use a very strong bath of potassium chromate without having an excess of chromium deposited on the fibre. In order to get chromium oxides equal to 1·5 per cent. of potassium bichromate deposited on the wool, the dyer may have to add each time 3 to 4 per cent. to the bath, because a considerable portion of it is converted into the less active form. A

* Knecht, *Journ. Soc. Dyers and Col.*, 1889, p. 184.

"chrome" bath which has been worked 15 or 16 times has been known to contain about 20 lbs. of chromate as such and as bichromate. It need not have contained more than 5 or 6 lbs., the quantity added for the first lot of wool. All that is necessary to prevent this accumulation and waste of chromate is to add sulphuric acid in the proportion to convert the neutral chromate into bichromate. The reaction takes place in accordance with the following equation:—

$$\underset{(389.)}{2K_2CrO_4} + \underset{(98.)}{H_2SO_4} = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

Practically, for every four parts of normal potassium chromate present in solution, one part of sulphuric acid should be added.

Direct Chrome Black.—If logwood liquor and a solution of potassium bichromate are boiled for some time a black precipitate is obtained, which may be collected and used for dyeing a *direct chrome black.* For this purpose the paste is mixed with water in a vat, and dissolved in oxalic acid, and the wool dyed in the solution one and a half to two hours. The results, however, are not as good as those obtained by Bonsor's black, where the bases copper and iron are used.

Woaded blacks are logwood blacks which contain more or less indigo. The name arises from the indigo being usually applied in what is called the "woad vat"—woad being one of the ingredients of the vat. But in whatever way the indigo is applied (except when indigo is dissolved in sulphuric acid) the goods are commercially known as woaded. After "woading," the material may be dyed up either by the "copperas" or "bichrome" method.

In the case of woaded chrome blacks, the indigo is sometimes applied after chroming in order to prevent loss of indigo, but the usual custom is to dye with indigo before chroming. This chroming must be done without acid, otherwise some of the indigo will be oxidised and destroyed. In light shades sometimes there is scarcely any indigo left after chroming.

The object of woading or indigo-dyeing is to give a black faster to light If a fair amount of indigo is used the colour is undoubtedly much superior; but, in many cases, the quantity of indigo put on is so little that its effect must be inappreciable. Many woaded blacks are better only in name than so-called common fast blacks. A chrome black dyed with logwood, fustic, and Alizarin red, where the chrome has been previously reduced to chromic oxide, is far superior to a great many of the woaded blacks, where logwood and fustic have only been used in addition to a little indigo.

Logwood blues are produced on wool much in the same way as chrome blacks—smaller quantities of mordant and dye being used, and the addition of fustic omitted. The amount of potassium bichromate should be reduced to a minimum, and it should be in the reduced state. The lighter the shade the more quickly, of course, any change is noticeable. A purplish shade is obtained by adding a little stannous chloride (about 1 per cent.) towards the end of the dyeing operation. The same effect is obtained, and with better results as regards fastness, by adding Alizarin red, Gallein, or Gallocyanin to the dye-bath. In some cases the wool is first dyed a light shade of indigo, as in woaded blacks.

Some dyers mordant with alum and tartar for logwood blues, using about 6 per cent. of alum or 4 per cent. of aluminium sulphate, and 6 to 8 per cent. of tartar. In such cases it is advisable to add either chalk or calcium acetate to the dye-bath unless the water already contains much lime.

Sometimes Water blue is added to the mordant-bath for brightening the ultimate colour.

Logwood purple is obtained by mordanting with about 4 per cent. of stannous chloride and 4 to 6 per cent. of tartar, and dyeing in a fresh bath

with 20 to 40 per cent. of logwood. The colour is not fast, and the same shade is easily obtained by more permanent dyes. Tin salts, furthermore, always give the wool a more or less harsh feel.

Dyeing of Silk.—Logwood is used in very large quantities for the black dyeing of silk, and it is fixed on this fibre principally on iron mordants; aluminium-, copper-, and tin-mordants are of minor, and chrome-mordants of no importance for the fixation of logwood on silk; nor is logwood used for the production of colours other than black on silk.

The black dyeing of silk is essentially different from the usual dyeing methods, since the intention is usually not only to impart a black shade to the material, but also to add to its weight; this increase may even be as much as four times the weight of the fibre itself (*i.e.*, 400 per cent.). The weighting is effected by the fixation of tannin-iron and tannin-tin lakes in the fibre; chestnut extract, gambier, pyrolignite, and "nitrate of iron," yellow prussiate of potash, and stannous chloride being the most important materials. When fixed in large quantities the tannin-iron lakes are by themselves sufficient to dye the silk fibre black; but for the production of fine black shades the dyeing is finished with the aid of logwood.

Black dyeing of silk may be divided into

I. Black on Raw Silk.
II. Black on Discharged Silk.
III. Black on Souple Silk.
IV. Black on Wild Silks.

I. *Blacks on Raw Silk.*—These are principally dyed on yarns which are intended to serve in pile fabrics, sateens, &c., as the basic of the fabric, and are visible on the back of the goods only. The silk is not boiled off, in order that the strength of the fibre may be preserved, and, consequently, hot soaping during the dyeing process is to be avoided. Yellow silks are sometimes bleached with aqua regia before dyeing.

Three different kinds of black on raw silk may be distinguished:—

1. Black with Chestnut Extract and Pyrolignite of Iron.
2. Black with Prussian blue.
3. Black with Logwood (without heavy weighting).

The process of dyeing black on raw silk with chestnut extract and black liquor is described under the heading of *Iron mordants on silk* (p. 268). It weights up to 200 per cent.

Hummel (*Dyeing of Textile Fabrics*) describes the following heavily charged black for fancy goods:—Dye raw silk black by alternate treatments with chestnut extract and pyrolignite of iron; after repeating these operations fifteen times the silk is weighted to about 400 per cent. Soften and brighten with 10 to 20 per cent. of olive oil, &c. In the first bath of chestnut extract the liquor is heated sufficiently to soften the silk-gum (*soupling*).

A finer black is produced by dyeing the silk blue with "nitrate of iron" and yellow prussiate of potash and topping with chestnut extract. If a heavy weighting is required the raw silk is treated about three times with "nitrate of iron" and subsequently with yellow prussiate, as described in the above-named chapter (p. 269). The silk thereby receives a charge of about 24 per cent.; each iron bath yielding 4 per cent., or altogether 12 per cent.; and the same amount is added by the subsequent conversion of the ferric oxide into Prussian blue. After a good washing in running water the silk is dyed black and weighted still more in a bath of chestnut extract; 150 per cent. of extract, 15° Tw. (of the weight of the silk), are used, and the material is worked in this bath at 40° to 45° C. for some time, whereby a weighting of 30 to 40 and

even 50 per cent. is added to that already produced, or 60 to 70 per cent. altogether. By repeating the whole treatment three times a weighting of more than 200 per cent. may be effected.

In cases where the material does not admit of being subjected to so many treatments a light black may be produced with logwood after the methods used for the so-called "English black" (on boiled-off silk).

Prepare a bath with—

50 to 60	per cent.	logwood,
25 to 30	,,	fustic,
4 to 5	,,	copperas,
1 to 2	,,	acetate of copper,

and sufficient water (20 times the weight of the silk). Dissolve the salts in the water, add the decoctions of the dyewoods and stir well. Work the silk in this bath for half an hour, lift and heat to 60° C., and work again for half an hour. Expose the silk which has now acquired a brownish colour on rods to the open air for one hour, rinse well, and hydro-extract. The bath is run off.

Work the silk for one hour at 50° C. in a decoction of 50 per cent. of logwood; then rinse well. The bath is not preserved.

Work for one hour in a tepid soap bath, containing 30 to 50 per cent. of good soap, wring, rinse in running water and hydro-extract; this treatment softens the silk and improves the shade. Brighten with a moderate amount of acid; vegetable acids or lime juice are most suitable.

II. *Blacks on Discharged Silk.*—The discharging of silk for black dyeing, especially for heavy blacks, requires great care in order that the goods may suffer as little as possible, and be able to resist the great number of operations they are subjected to.

A great many different methods of black dyeing discharged silk are known; the following are the most important processes:—

1. English black (light black).
2. Blacks for Pile Goods (not weighted).
3. Lyons black (with Prussian blue; moderately weighted).
4. Mineral black (moderately weighted).
5. Tin weighted blacks.
6. Heavy black (with Catechu and Tin Crystals).
7. Heavy black (with Acetate of Lead; very heavily weighted).

1. *English Black.*—This black is principally used for tender materials, which do not allow a great number of treatments, or which are to be woven together with white yarns.

Dye with—

50	per cent.	logwood,
50	,,	fustic,
5 to 6	,,	copperas, and
2 to 3	,,	acetate of copper,

half an hour at 50° to 60° C., lift and heat to 70° C., and work half an hour more; run the dye-liquor off and allow the yarns, which now possess a brownish colour, to hang one hour on the rods in the dye-vat; after this rinse well. Dye in a fresh bath with 50 per cent. of logwood and 50 per cent. of soap; enter at 50° to 60° C., turn half an hour, lift and heat to 70° to 75° C., and turn another half hour. Run off the liquor and rinse first in the dye-vat and subsequently in running water; hydro-extract. Soften and brighten with 2 to 4 per cent. of oil which has been mixed with sufficient acid to give a slightly sour taste.

A fine greenish-black is thus produced without any weighting of the silk.

If an increase of the weight is required the silk may be treated once or

several times with "nitrate of iron" in the manner described on p. 270 for boiled-off silk. By three treatments 12 per cent., or one-half of the loss the silk suffers by the discharging process, may be recovered; a further weighting with "nitrate of iron" would injure the material on account of the destructive influence of the ferric salt on the silk fibre. A light bath of catechu at 50° to 60° may follow, and then the silk is dyed and finished precisely as in the preceding method. The mordanting with "nitrate of iron" imparts to the goods a fuller and less greenish tone which even becomes bluish if a smaller amount of fustic is used.

2. *Blacks for Pile Goods* (*without weighting*).—Black velvets and plushes are desired to appear bluish-black when viewed direct or "underhand" and black-blue when viewed through or "overhand." This effect is produced by mordanting with alum and by dyeing without fustic.

Work for some time in a cold concentrated solution of alum, steep overnight, and rinse next morning in calcareous water. Dye as for "English black," first with 50 per cent. of logwood, 3 to 4 per cent. of acetate of copper, and a little copperas, and subsequently in a soap-bath with logwood; less copperas than for "English black," and no fustic is used. No scroop being desired for pile goods, the yarns are turned a few times in a weak tepid bath of neutral soap for softening, hydro-extracted, and dried without rinsing. Lustreing of the yarns in the moist state is avoided, since it deepens the colour too much. The material is sometimes dyed with Methyl violet or Aniline blue before the mordanting, to produce a finer bluish tone; great care is necessary that the dyestuff be not stripped by the subsequent treatment.

Like the English black this black does not increase the weight of the silk.

3. *Lyons Black* (*Black with Prussian blue, moderately weighted*).—Mordant two or three times with "nitrate of iron," soap, and dye blue with yellow prussiate of potash (p. 266). A weighting of 16 to 24 per cent. is obtained; or by a three-fold treatment with nitrate, &c., the loss sustained by the discharging is recovered and the silk brought to "pari." A further weighting of 4 per cent. may be added by one more treatment with "nitrate of iron" after the blue dyeing, and subsequent rinsing with water to precipitate the ferric hydroxide (hot soaping would affect the Prussian blue). Work the silk after these treatments one hour in an old bath of catechu (gambier) standing at 4° to 7½° Tw., the temperature of which should not exceed 50° C., so that the Prussian blue may not be decomposed and the shade become too dark; rinse and hydro-extract. The silk acquires in the catechu bath an overcharge (over pari) of 15 per cent. and becomes more greenish. For the weighting of silk pale cutch (gambier) is used, since dark cutch does not yield satisfactory results, the colours not resisting the action of soap. Experience has proved that old baths of catechu give better results as to shade and to weight than new ones; they are maintained at the same specific gravity (and strength) by regular additions of fresh solutions of catechu. To obtain a more bluish shade work in a cold concentrated bath of alum and rinse in water. Dye exactly as for English black (p. 342), first with logwood, fustic, copperas, and acetate of copper, and subsequently with logwood and soap. On account of the preceding aluming, however, great care is required to avoid uneven dyeing, and 100 per cent. of a very fatty soap (calculated on the weight of the silk) are required for the second dye-bath. Enter at 50° to 60° C., and heat very gradually to 80° to 85°; the heating may last five to six hours. After the dyeing is finished run off the liquor, rinse first in a dye-vat with soft water and then in running water. Brighten with 4 to 6 per cent. of good olive oil and lime juice, and finally lustre.

This black possesses a very fine bluish tone, and gives 5 to 15 per cent. weight above "pari."

4. *Mineral Black.*—This black gives a moderate weighting (about 30 per cent.); it is inferior to the preceding black in fineness of shade. The operations required are three or four treatments with "nitrate of iron," blue dyeing with yellow prussiate of potash, hot catechuing, dyeing with logwood and soap (as for English black, p. 342), brightening and lustreing. For catechuing, the silk is worked one hour at 70° to 75° C. in an old bath of catechu (gambier) (4° to 7½° Tw.) which is used continuously. Catechu acts at the elevated temperature on Prussian blue, and is fixed in large quantities, adding a weighting of 25 to 30 per cent. to the charge already obtained by the preceding treatments, which may be as high as 36 per cent.; hence this method produces a weighting of 50 to 60 per cent., or an overweight above "pari" of 25 to 35 per cent. After the catechuing follow the dyeing with logwood and soap, softening, brightening, lustreing, exactly as for English black. The shade produced is a very full greenish-black.

The following black is very similar; but it possesses a better, more bluish shade, and yields about 6 per cent. more weight. It differs by the special treatment with pyrolignite of iron and the subsequent catechuing, and consists of the following series of operations: two, three, or four treatments with "nitrate of iron," blue dyeing with yellow prussiate, one more treatment with "nitrate of iron," hot catechuing, mordanting with pyrolignite of iron, tepid catechuing, dyeing with logwood and soap, brightening and lustreing. For the tepid catechuing, after the first mordanting with pyrolignite of iron, sometimes a dyeing with logwood without soap is substituted to obtain a more bluish-black. The pyrolignite bath is used at a specific gravity of 3° to 4½° Tw., and at a temperature of 20° to 30° C.; the silk is turned half an hour, rinsed, and worked half an hour in an old tepid catechu bath (7° to 8° Tw.); the pyrolignite bath and the catechu baths are used continuously. The other operations are exactly the same as for the preceding "mineral black."

5. *Tin Weighted Black.*—In spite of the high price of tin and its compounds, the tin-phosphate-silicate process (see p. 278) has latterly come into more or less general use for the weighting of black silks, partly owing to its giving superior results, and partly owing to the fact that by this means the weighting can be effected in a smaller number of operations, and consequently more economically than by the old-fashioned iron process.

A process for obtaining a blue-black on tin weighted silk is described in Weidmann's U.S. Patent No. 780,924, 1905,* and the mode of working may be ascertained from the following abridged description:—

The boiled-off silk is weighted in the ordinary way with tin, with proper washings. It is then treated in a bath with dilute acetic acid, and afterwards in black iron liquor at suitable strength for the usual time. After wringing and washing, it is placed for two to three hours in the old black iron gambier bath, which consists of gambier in which the silk coming from the black iron has been worked. This bath should be strengthened with fresh gambier, 30 to 50 per cent. logwood extract, and 40 to 60 per cent. fustic extract, and brought up to 70° C. The silk is finally washed, and dyed to shade in a bath containing logwood extract and soap, heating until the desired shade is obtained. It is then washed, and treated with oil and acid as usual.

More exact particulars are given in Knup's English Patent No. 6,728, 1904.† According to this method, a 16- to 18-oz black (10 per cent. weighting) is obtained on boiled-off silk as follows:—

The silk is immersed in a solution of stannic chloride at 53° Tw. for one hour in the cold, then washed and worked in a solution of phosphate of soda at 6° Tw. for one hour at 65° C., then washed and worked in a solution of

* *Journ. Soc. Dyers and Col.*, 1905, p. 77.
† *Ibid.*, 1904, p. 251.

silicate of soda at $4\frac{1}{2}°$ Tw. for one hour at 50° C.; then washed and worked in a solution of 14 per cent. acetic acid. The silk is then worked in a solution of black iron of 77° Tw. at 15° C. for one hour, wrung, covered for two hours, then washed and worked in a solution of 100 lbs. gambier for 100 lbs. silk, to which 20 lbs. logwood extract and 40 lbs. fustic extract are added, for two hours at 70° C. It is then washed and dyed in a bath containing 20 lbs. logwood extract and 50 lbs. soap per 100 lbs. silk, being entered at 43° C., and the dyeing being continued with a rising temperature until the desired shade is obtained. A good blue-black is generally obtained at about 65° C., but this varies according to the nature of the silk and the difference in the weighting process. After the desired shade is obtained, the silk is washed and finished with 2 gallons lemon juice and $1\frac{1}{2}$ lbs. oil for 100 lbs. silk.

A 30- to 32-oz. black (100 per cent. above "pari") is obtained by working the silk in—

1. Stannic chloride, 53° Tw.
2. Phosphate of soda, 6° Tw., 65° C.
3. Stannic chloride, 53° Tw.
4. Phosphate of soda, 6° Tw., 65° C.
5. Stannic chloride, 53° Tw.
6. Phosphate of soda, 6° Tw., 50° C.,

then in a bath containing 14 lbs. acetic acid for 100 lbs. of silk at 20° C. After this the silk is worked in the black iron solution, and the rest of the process is the same as in the first example.

6. *Heavy Black with Catechu and Tin Crystals.*—This method yields a weighting up to 80 and even 100 per cent.; it produces a good shade, but the weighting is effected at the expense of the strength of the fibre. The peculiarity of this process is the application of catechu and tin salt; the other operations resemble those which have been described in the preceding section.

Mordant 6 to 8 times with "nitrate of iron," soap, and dye blue with yellow prussiate; each mordanting yields 4 per cent. weight, and 6 or 7 treatments would give 24 to 28 per cent.; this result is doubled by the blue dyeing so as to produce a weighting of 48 to 56 per cent., or an overweight above "pari" of 24 to 30 per cent. Prepare a fresh bath of gambier (100 to 150 per cent. of the weight of the silk) in a dye-vat of suitable dimensions which admits of working 300 lbs. simultaneously, keeping, however, the hanks closely together to prevent access of air as far as possible; work the yarn half an hour at 50° C., lift, heat to 70° to 80° and add a solution of 8 to 12 per cent. tin crystals (of the weight of the material). By the addition of tin crystals the bath changes from brown to yellow and is partially precipitated; work the yarn again for one or two hours and allow to rest in the bath overnight or longer. The material will not be injured by remaining in the bath for several days if it is prevented from rising to the surface. Some dyers enter the catechu solution at a higher temperature than 50° C., or even at the boil, and obtain a heavier weighting by the powerful action of the catechu on Prussian blue. After taking the yarn out of the bath rinse well in water and run off the catechu liquor; after settling, the clear liquor may be used again for this operation, whilst from the sediment tin may be recovered (see p. 278). The silk changes by the preceding treatment from blue to a dull green, and acquires a harsh feel. Soften by working one hour at 50° to 60° C. in a bath containing 33 or even 50 per cent. of soap, then rinse and hydro-extract whilst the soap bath is run off. Work the silk in another bath of catechu (100 per cent.) one hour at 70° to 75° C., rinse and hydro-extract; preserve the bath. Dye with 50 per cent. of logwood and 50 to 60 per cent. of soap, first half an hour at 50° to 60° C., and then at 70° to 75° until the desired shade is produced. By the com-

bination of the purplish shade of the logwood-tin lake and of the above-mentioned greenish-black tone, a violet shade of black is obtained.

The weighting depends to a great extent on the mordantings with "nitrate of iron" in the beginning of the operation; the first two mordantings allow of a weighting of altogether 45 per cent.; the following mordantings are less effective and admit only 10 to 15 per cent. increase each; thus about 110 per cent. weighting, or an overweight of 85 per cent. above pari are obtained ultimately, if the silk was treated seven times with "nitrate of iron."

The reddish tone of this black may be changed to a more bluish and finer shade by a treatment with pyrolignite of iron, precisely similar to that described for mineral black (p. 344). After the second catechuing, work the silk for one half hour to one hour in a weak bath of pyrolignite of iron, rinse, hydro-extract, turn for half an hour in an old bath of catechu (4° to 7½° Tw.) at a temperature not exceeding 50° C., and, after draining, rinse and hydro-extract; this treatment effects also a weighting of 4 to 5 per cent. Dye as before; if the goods should become reddish, heat to 80° to 85° C., and, if necessary, add some soap; finally run off the liquor, rinse the silk first in the dye-vat and subsequently in running water, hydro-extract, and brighten with 6 to 8 per cent. of acidulated oil emulsion. The silk is ultimately finished by lustreing.

A further increase of the weight may be effected by treating the silk after dyeing and washing (1) in a weak bath of catechu at 50° C., (2) steeping in pyrolignite of iron, (3) again in catechu at 50° C., and (4) dyeing with logwood and a large amount of soap; these four operations may even be repeated in the order given.

7. *Heavy Black* (*weighted to* 350 *per cent.*) *with acetate of lead* is described by Moyret. It is also used for fancy goods, the raw material of which is waste silk. Discharge in soap at the boil or at 60° to 70° C.; soak in 150 per cent. of chestnut extract 15° Tw., at 40° to 50° C.; rinse; work in pyrolignite of iron at 60° to 70° C.; repeat the treatments with chestnut extract and black liquor according to the desired weighting up to six times, increasing the amount of chestnut extract gradually up to 250 per cent.; six treatments yield a weighting of 250 per cent. After this pass through a bath of basic acetate of lead which has been prepared by saturating a solution of pyrolignite of lead, 8° to 15° Tw., with litharge; in this bath the silk is weighted about 100 per cent. more, extracting a corresponding amount of lead oxide from the bath.

The previously described methods for increasing the weight of the silk, such as treatment with "nitrate of iron" and yellow prussiate or with gambier and tin crystals, may also be employed to attain a higher charge.

III. *Black on Souple Silk.*—The soupling of silk for black does not precede the dyeing, but forms part of the dyeing itself. Mordant the raw silk two to six times in "nitrate of iron," taking care that the bath remains sufficiently basic; the raw silk possesses a direct affinity for ferric oxide, and extracts it from the bath, leaving free acid behind, whereas boiled-off silk absorbs the salt without dissociation; dye blue with yellow prussiate. The next operation is the soupling with a tannin, such tannins as give blue colourations with ferric salts being employed, notably tannic acid, extract of gall-nuts, myrabolans, and divi-divi. Work in a solution of the tannin (standing at 6° to 8° Tw.) at 50° C. for half an hour, lift and heat to 70° C., work again, and so on several times, raising the temperature gradually to 90° or 95°; this operation lasts from two to five hours, and finally the goods may be left in the bath overnight. The tannin-bath is used continuously. Some stannous chloride (8 to 15 per cent., more or less, according to the number of mordanting treatments with "nitrate of iron") may be added to the tannin-bath on heating the first time; the same precautions as

to access of air as usual are required, and the bath is finally run off. The further operations are similar to those used for the dyeing of boiled-off silk, for instance, to those described for the production of mineral black (p. 344). They consist chiefly in dyeing with logwood in a soap-bath with or without mordanting with pyrolignite of iron immediately after the soupling. In dyeing souple silk care must be taken, however, never to raise the temperature of the soap-bath above 50° C., not to dissolve the silk gum. The weighting of the silk may be increased to 80 and even 100 per cent. By repeated treatments of the soupled silk with "nitrate of iron," chestnut extract, tin crystals, and prussiate of potash, even double this amount may be reached. The weighting of souple silk is more complicated than that of raw or discharged silk, is principally a matter of experience, and cannot be well described.

IV. *Black on Wild Silks.*—The wild silks offer difficulties in dyeing generally, and still more so in black dyeing, since they do not take up colouring matters easily, and still less so iron mordants.

Moyret (*l.c.*) recommends the following process for black dyeing of tussur:—Discharge with dilute caustic soda at 60° to 80° C. Mordant once or twice in "nitrate of iron" and fix with caustic soda. Dye blue in a weak bath of yellow prussiate of potash. Work in a weak bath of chestnut extract, and pass through pyrolignite of iron; repeat these last two operations twice (not for weighting, but for saddening the shade). Dye in logwood and soap and brighten with 6 to 8 per cent. of olive oil.

Detection of Logwood on Dyed Fabrics.—The detection of logwood on dyed fabrics when other colouring matters are absent is a comparatively simple matter; but in many compound shades its presence can only be discovered by the employment of numerous delicate tests. The information generally given on this subject refers, as a rule, only to the pure colouring matters; but, in many cases, these reactions are of little help. However, in the first place, the pure colouring matter should be studied, and all reactions carefully noted. The detection of the mordant which has been used often throws much light on the kind of colouring matter which may be present. If no mordant is present on the fibre one may safely exclude all the adjective dyes, such as logwood, &c. In order to test for the inorganic mordants a portion of the fabric is ignited in a platinum or porcelain dish, and the ash which remains, free from carbon, treated as follows:—

Chrome Mordants.—Ash, yellowish or brownish-green. Add a little potassium chlorate and fuse—a bright yellow mass obtained. If dissolved in water and acetic acid, and acetate of lead added, a yellow precipitate is obtained, confirming the presence of chromium. If a trace of chromium is present *it may be* detected by means of a borax bead, which acquires a green colour in the presence of chromium.

Iron Mordants.—Ash, reddish-brown colour. Dissolve in hydrochloric acid, add potassium ferrocyanide; a blue precipitate indicates iron.

Copper Mordants (usually found in combination with iron and sometimes with chrome).—Dissolve the ash in hydrochloric acid, add a slight excess of ammonia, and filter. If much copper is present the filtrate will be blue. Smaller quantities are detected by adding acetic acid and potassium ferrocyanide, which produces a reddish-brown precipitate or colour.

Aluminium Mordants.—Ash, white. Dissolve in hydrochloric acid and add ammonia, which gives a white precipitate in presence of alumina. Confirm by heating on charcoal with cobalt nitrate; a blue mass is thus obtained.

Tin Mordants.—Ash, white; yellowish when hot. Globules of tin are obtained by heating on charcoal; small quantities detected by the red colour imparted to a borax bead containing a trace of oxide of copper when heated in the reducing flame.

A Logwood blue or black gives the following reactions with the more common reagents:—

Reagent.	Chrome Mordant.	Iron Mordant.
Hydrochloric acid, sp. gr. 1·16, .	Red-violet (slowly).	Crimson, more easily extracted.
Sulphuric acid, sp. gr. 1·84, . .	Olive-brown, yellow on dilution.	Olive-brown, yellow on dilution.
Sodium hydrate, 10 per cent., . .	Slowly violet.	Quickly violet.
Ammonia (strong), ...	Little action, very slowly violet.	Little action, very slowly violet.
Stannous chloride, Hydrochloric acid, Water (equal parts), ...	Red-violet.	Light red.

The above tests are all made in the cold, and may be conveniently performed in porcelain basins. Boiling alcohol has no effect upon a logwood colour, neither has a boiling solution of soap nor a ½ per cent. solution of sodium carbonate. Boiled with dilute hydrochloric or sulphuric acid (5 per cent.) the logwood is more or less removed and the solution becomes red or orange-red. The fibre is of a light purple or reddish-drab colour. On adding an excess of caustic soda to the acid solution, the latter is immediately turned to a deep violet colour, which, however, gradually disappears with the formation of a brown precipitate, while the solution also remains tinted brown. If this test is made with a Logwood black, blue, or violet, which contains Alizarin red, the alkaline solution remains purple or violet after the logwood has been precipitated. On now adding a dilute acid the purple or violet colour, if due to Alizarin red, will turn to a light yellow. Dark fast navy blues on wool are frequently dyed either with indigo, Alizarin blue, or Gallocyanin, and logwood is often used in conjunction with them, being very much cheaper. In some cases this is permissible, but in others, customers object to the use of logwood altogether in such shades. Consequently, the detection of logwood in the presence of these colouring matters is a matter of some importance. With indigo its detection is easy; but the presence of a small amount of logwood with Alizarin blue and Gallocyanin cannot be so readily ascertained. The following method can be recommended. It is exceedingly simple, but requires close observation. It depends on the action of cold concentrated sulphuric acid. This reagent gives with logwood, as already stated, a brownish-red solution, which becomes yellow on dilution with water. It gives, with Alizarin blue, a deep violet-blue liquid, which becomes red-violet on dilution; with Gallocyanin, a violet liquid, which becomes redder on dilution; and with indigo, at first green, then deep blue, which remains blue on dilution. The colour of the diluted solution is more clearly seen after filtering. The yellow colour of the logwood is more intense than the other solutions, and a very small amount is sufficient to modify their shade. The delicate pink given by Gallocyanin and Alizarin blue becomes red, orange-red, orange to orange-yellow, according to the amount of logwood present. In a mixture of indigo and logwood, the colour of the liquid is green after adding sulphuric acid and diluting with water, but on passing the solution two or three times through a filter the indigo is retained and the logwood only is obtained in the filtrate. This reaction is of importance, since it enables one to distinguish between logwood, Gallocyanin, and Alizarin blue in the presence of indigo; which, otherwise, would be a very difficult problem. Logwood is at once detected in an indigo-dyed fabric by boiling with a 5 per cent. solution of sulphuric acid, which removes the logwood, as

previously stated. Gallocyanin, if present, would also be partially removed. After repeating the operation once or twice, the colour remaining shows approximately the depth of indigo present in such a mixture, but, if the wool contains chromium in the form of a chromate, a portion of the indigo will have been destroyed by the chromic acid liberated during the reaction. It should also be remembered in applying this test that several blue colouring matters besides indigo are unaffected, or only slightly affected, by boiling acids. Cloth dyed with indigo and logwood colours hydrochloric acid *red*, and a 10 per cent. solution of caustic soda *violet;* whereas pure indigo gives up no colour to either liquid. The ash of wool or cotton fabrics dyed with logwood and indigo will contain either chromium or iron, or both; whereas pure indigo will contain neither, or, at most, a trace of iron.

FUSTIC.

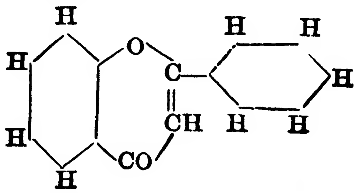
This dyestuff is also known as old fustic, Cuba wood, and yellow wood. It is the wood of a tree belonging to the natural order *Urticaceæ*, known botanically as *Morus tinctoria* or *Maclura tinctoria.* It is a native of Brazil, Mexico, and several of the West Indian Islands, the best qualities being produced in Cuba and Tampico.

According to most authorities, fustic contains two colouring matters, which were first isolated by Chevreul. One is readily soluble in water, which Chevreul named *morin jaune*, and the other, which is nearly insoluble, he called *morin blanc.* If a concentrated syrupy aqueous decoction of fustic is allowed to remain at rest for some days, an abundant crystalline deposit is formed. Commercial fustic extract will answer the purpose. The crystalline deposit is washed rapidly with a little cold water and strongly pressed. The product is then boiled twice with water, which yields a solution containing morintannic acid and a residue of *morin* and morate of lime. The aqueous solution is concentrated by evaporation, and the morintannic acid precipitated by the addition of a little hydrochloric acid. The product is recrystallised two or three times from an aqueous solution acidulated with hydrochloric acid. In order to isolate pure moric acid the residue, which is insoluble, or nearly insoluble, in water, is treated with dilute hydrochloric acid (to decompose the calcium morate), and dissolved in alcohol. On the addition of two-thirds of its bulk of water the solution deposits moric acid in the form of yellow needles, which may be further purified by repeated crystallisation from weak alcohol.

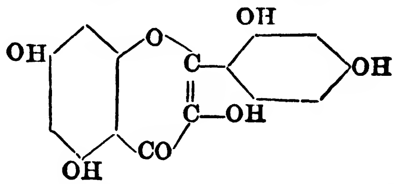
Morintannic acid (which is also known as *Maclurin*) is deposited from its solution in the form of a light yellow crystalline powder composed of microscopic needles. It is soluble in 64 parts of cold, and 2·14 parts of boiling water, and is also readily soluble in alcohol, wood spirit, and ether. The ethereal solution is fluorescent, being greenish by reflected, and brown by transmitted light. It melts at 200° C., gives off water and acid vapours at 250°, and completely decomposes at 270°. The composition of morintannic acid is $C_{13}H_{10}O_6$ or $(OH)_3C_6H_2 . CO . C_6H_3(OH)_2$. When heated with a strong solution of caustic alkali it yields phloroglucin and protocatechuic acid. Morintannic acid dissolves in cold concentrated sulphuric acid with a yellow colour, and is reprecipitated on the addition of water. The strong acid solution, if allowed to remain at rest for some days, deposits brick-red crystals of rufimoric acid. A solution of morintannic acid, treated with zinc and sulphuric acid, assumes at first a red colour which turns slowly to orange. The solution then contains phloroglucin and machromin; the latter crystallises in slender needles, and becomes blue on exposure to the air. Hydrochloric acid gives a blue precipitate and the alkaline solution also becomes blue on exposure to the air. Ferric chloride added to a solution of machromin produces a fine violet colour

which gradually passes into blue. A solution of morintannic acid gi es a yellow precipitate with *gelatin*, a greenish precipitate with *ferroso-ferric sulphate*, a yellow with *acetate of lead*, and yellowish-red with *stannous chloride*.

According to the investigations of J. Herzig, St. v. Kostanecki, A. G Perkin and others, morin, fisetin, luteolin, quercetin, rhamnetin, and some other natural yellow mordant dyes are hydroxy derivatives of the cyclic compound flavon, which is represented by the constitutional formula—



The constitution of morin has been shown to be



according to which it is represented as one of the tetrahydroxy derivatives. It is remarkable that, though a strong mordant dye, it does not follow Liebermann and Kostanecki's rule, inasmuch as it does not contain two hydroxyl groups in the ortho position to each other.

Morin is nearly insoluble in cold water, and is only slightly dissolved by boiling water. It requires 4,000 parts of water at 20° C., and 1,060 parts at 100° C. to dissolve it. It dissolves readily in strong alcohol, from which solution it is reprecipitated on the addition of water. It is insoluble in carbon bisulphide, and only slightly soluble in ether. It combines with, and is dissolved by, alkalies, forming a yellow solution, from which it is precipitated by acids. Ferric chloride added to an alcoholic solution of moric acid produces an olive-green colouration.

A solution of an alkaline morate, treated with sodium amalgam, at first becomes blue, then green, and finally yellowish-brown.

A solution of morin is not precipitated by gelatin although it stains animal matter yellow.

W. M. Gardner* has compared the dyeing properties of morin and morintannic acid. He finds morin to give considerably deeper shades with chromium and aluminium mordants, but lighter shades with iron mordants than morintannic acid.

A decoction of fustic gives the following reactions :—

Alkalies, ...	Orange-yellow to yellow-brown colour.
Weak acids, . . .	Slight pale yellow precipitates.
Alum, ...	Bright yellow precipitate.
Acetate of lead, . .	Yellow-orange precipitate.
Acetate of copper, . .	Brownish-yellow precipitate.
Ferrous sulphate, . .	At first, olive colouration ; on standing,
Ferric sulphate, . .	a dark brownish-olive precipitate.
Stannous chloride, . .	Rich brown-yellow precipitate.
Copper sulphate, . .	Dark green precipitate.
Gelatin, ...	Yellow flocculent precipitate.

* *The Dyer*, 1892, p. 46.

Fustic is used in the dye-house in various forms; as chipped and rasped wood; as an aqueous extract; as a paste; and, to a certain extent, as a dry or solid extract.

Fustic is one of the most important of all natural yellow colouring matters, especially for wool and worsted, but has been replaced to a large extent by artificial dyestuffs, such as Anthracene yellow, Alizarin yellow, Mordant yellow, &c. It is very extensively used in conjunction with logwood for dyeing black, and together with logwood, Alizarin red, and other colouring matters, for numerous compound shades—*e.g.*, browns, olives, drabs, &c. In all such cases the general mordant is bichromate of potash or soda. For the production of bright yellow shades *tin* or *aluminium* mordants are used. These bright yellows, however, although fairly fast to milling, are soon changed on exposure to light. They become much browner. Fustic gives the following series of shades with the various mordants:—

Chromium mordants, . .	Olive-yellow to brownish-yellow.
Aluminium, ...	Yellow.
Iron, ...	Dark olive.
Copper, ...	Olive.
Tin, ...	Bright yellow to orange-yellow.

Fustic, like logwood, is sold as *chipped* or *rasped wood*, and as a solid or liquid extract. After chipping or grinding, the wood is usually "matured" or "aged" in the same way as logwood—*i.e.*, it is spread in layers on a floor, and, after being well moistened, it is allowed to remain several weeks, the mass being remixed at intervals.

In the case of logwood, the essential action of the ageing process is the oxidation of *hæmatoxylin* into *hæmatein*, but no similar change takes place in the case of fustic, and the only useful benefit the process appears to confer is the somewhat incidental one of thoroughly soaking the wood and thus rendering the colouring matter more susceptible to extraction in the dye-bath.

Fustic extracts are manufactured in the same way as logwood extracts (see *Logwood*). The liquid extract is usually said to be of a strength of 51° Tw., but consisting, as it does, of a lower layer of insoluble morin, upon which rests a pasty solution of maclurin, the true specific gravity is not easy to determine.

Dyeing of Cotton.—Fustic is applied to cotton much in the same manner as logwood. It is used principally for compound shades. Fustic as a yellow is not much employed for cotton, and where formerly used has been superseded by Chrysamin and similar dyes. Fustic is of considerable use in the dyeing of catechu shades.

Dyeing of Wool.—In the heavy woollen district fustic is used in very large quantities in conjunction with logwood, indigo, and Alizarin colours. In such cases the mordant is invariably bichromate of potash, although ferrous sulphate is often used as a saddening agent. The bichromate of potash is applied to the extent of from 2 to 4 per cent. previous to dyeing, as already described under logwood. When the red woods are used for fast browns, which, however, is now not often the case, the bichrome is applied after dyeing. In such cases considerably more fustic is required to produce a given shade than where the wool is mordanted before dyeing. In the dyeing of drabs and browns with fustic, logwood, madder, &c., it is customary to use a little sumach. The principal object appears to be that in conjunction with copperas it helps to sadden the shade, but its utility is questionable. The tannin which it contains imparts a harsh feel to the wool, and, furthermore, interferes with the dyeing properties of logwood. Taking all things into consideration, fustic dyed upon a chromium mordant is still regarded by some as the best yellow colouring matter which the dyer possesses. It is fast to milling and soaping, and

stands light well. On exposure to light the shade becomes browner, but in many compound shades the change is not readily noticeable. The so-called Alizarin yellows, Galloflavin, &c., are certainly not superior in this respect. Fustic yields the brightest shade with stannous chloride as the mordant. Either separate baths or one bath may be used, as in the case of cochineal. The single bath method gives the best results. A good yellow is obtained with 4 per cent. of stannous chloride, 4 per cent. of oxalic acid, and 50 per cent. of fustic. The addition of a little gelatin is beneficial, since it precipitates the tannin of fustic, and thereby yields brighter shades. A larger quantity of tin salts gives still brighter yellows, but it is objectionable on account of the harsh "handle" which the wool acquires. In practice these bright yellow shades are now seldom dyed with fustic or other natural yellow colouring matters, these having been almost entirely replaced by artificial dyestuffs.

Dyeing of Silk.—Fustic is seldom used in silk dyeing for the production of yellow shades, but it finds application for shading certain blacks (see p. 342), as well as for olives and browns. It is fixed on silk with iron and copper mordants.

Detection on the Fibre.—In most cases where fustic has been used, the ash will contain chromium. In bright yellows or oranges tin will be found.

The reactions of fustic on the dyed fibre are not very striking, and are very similar to those of quercitron bark and Persian berries.

The following table shows the principal reactions of fustic dyed with chromium and tin mordants respectively:—

Reagent.	Wool Mordanted with Chromium Salts.	Wool Mordanted with Tin Salts.
Hydrochloric acid, . .	*Nil.*	Yellow solution; colourless on dilution.
Sulphuric acid, . . .	Little change, solution yellow; on dilution, fibre much lighter, solution colourless; ethereal extract shows green fluorescence.	Solution yellow; which remains yellow on dilution.
Nitric acid, ...	Brown; on addition of soda, red.	Brown; on addition of soda, red.
Stannous chloride, hydrochloric acid, and water, .	Little action.	Little action.
Caustic soda, . . .	Fibre brown; solution colourless.	Browner; solution yellow, decolourised on addition of HCl.
Boiling alcohol, . . .	*Nil.*	*Nil.*
Boiling soap, 1 per cent. solution, ...	Solution faintly yellow; fibre redder.	Solution deeper yellow; fibre straw colour.
Boiling sodium carbonate, ½ per cent. solution, . .	Solution orange-yellow; fibre redder.	As with soap.
Boiling 5 per cent. solution of sulphuric acid, . .	Solution yellow; fibre much lighter.	Solution yellow; fibre not greatly affected.

The presence of fustic in many compound shades can only be detected with great difficulty. In many cases its presence may be inferred by negative tests and a knowledge of the other constituents present. In the case of a brown,

for example, in which logwood and Alizarin red have been found, if the colour is fast to soap, gives up nothing to alcohol, and shows no characteristic reactions with other reagents, the yellow part of the shade is probably fustic. If the material is boiled in acetate of alumina it yields a yellow solution with a green fluorescence. The solution on evaporation with nitric acid becomes red.

Fustin or Wool Yellow is the commercial name of a paste dye obtained by treating the colouring matter of fustic with diazobenzene chloride. It dyes wool either mordanted or unmordanted, and either in a neutral or an acid bath. The shades are "redder" than those given by fustic and are not so fast to light

QUERCITRON BARK AND FLAVIN.

Quercitron Bark is the inner bark of a species of oak, the *Quercus nigra* or *Quercus tinctoria*, a native of America. It grows abundantly in Pennsylvania, Georgia, and the Carolinas. The best qualities are imported from Philadelphia, New York, and Baltimore. Bancroft, in 1775, first made known the dyeing properties of quercitron bark, and by an Act of Parliament obtained exclusive right of importing it for a period of six years.

The bark is removed from the tree, dried, ground between mill-stones, and comes into the market as a mixture of woody fibre and fine powder, of a yellow or buff colour. As a rule, the more of the fine powder present, the greater the value of the sample, since the woody portion, which is not easily reduced to powder, contains only a small quantity of colouring matter.

The colouring principles of quercitron bark are known as *quercitrin* and *quercetin*, and were first investigated by Chevreul. He also found it to contain a peculiar tannin, which has since been named quercitannic acid.

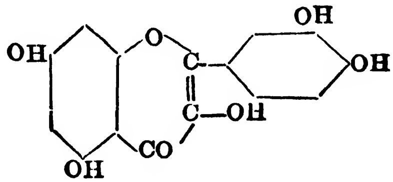
Quercitrin, $C_{21}H_{22}O_{12}$, may be obtained in the pure state by boiling quercitron bark with alcohol and precipitating the tannin by means of gelatin. The solution is then concentrated by evaporation, and the crystals which separate recrystallised from boiling alcohol. It may also be easily prepared from some varieties of flavin which consists of nearly pure quercitrin. On boiling with water and filtering, the solution on cooling deposits quercitrin in the crystalline form.

Quercitrin forms pale yellow crystalline needles possessing a feeble acid reaction. It is but slightly soluble in cold water, but dissolves more freely in boiling water. It is nearly insoluble in ether, but readily soluble in alcohol. Alkaline solutions dissolve quercitrin readily with a greenish-yellow colour, which becomes brown on exposure to the air. An aqueous solution gives bright yellow precipitates with acetate of copper and lead and with stannous chloride.

Quercitrin is a glucoside, and when boiled with dilute sulphuric acid splits up into quercetin, and a species of sugar, rhamnose. The reaction may be represented by the following equation:—

$$C_{21}H_{22}O_{12} + H_2O = C_{15}H_{10}O_7 + C_6H_{14}O_6.$$

Quercetin, $C_{15}H_{10}O_7$, having the constitution—



crystallises in needles of a bright yellow colour. It is insoluble in cold, and only sparingly soluble in hot water, but readily dissolves in alcohol and in acetic acid. It is very sparingly soluble in ether. It dissolves in alkalies with a deep orange-yellow colour, which becomes dark brown on being treated with sodium-amalgam. An alcoholic solution of quercetin gives orange precipitates with salts of calcium, barium, and lead. When dry quercetin is treated with concentrated sulphuric acid it forms a sulphonic acid, and the solution on dilution dyes wool a yellow without a mordant.

A freshly-made decoction of quercitron bark is transparent and of a dull orange-red colour, but in a short time it becomes turbid and deposits a yellow crystalline mass. The supernatant liquid acquires at the same time a redder colour, and the colouring matter is gradually destroyed. This decomposition is probably brought about by a ferment which splits up the glucoside. A decoction of quercitron bark, consequently, should only be prepared as required for immediate use.

Flavin is the name given to a preparation of quercitron bark. It is very much stronger, and yields brighter shades than the original bark. It comes into the market in the form of a very fine powder of a buff or brown colour. Flavin varies considerably in composition, according to the mode of preparation. It consists, as a rule, of a mixture of quercitrin and quercetin, with more or less woody fibre; but some specimens consist of nearly pure quercitrin, while others contain quercetin only. The best qualities of flavin are imported from America, where it is probably prepared from the fresh bark; but the details of the manufacture are kept secret. One method of preparation consists in boiling 100 parts of ground quercitron bark with 300 parts of water and 15 parts of sulphuric acid for some hours. After cooling, the mixture is run on to woollen filters, and the paste washed until free from acid. It is then dried and ground. The tinctorial power of good flavin is 12 to 20 times as great as that of quercitron bark.

In addition to the preparation flavin, quercitron bark is also used by the dyer in the form of extracts.

Dyeing.—Quercitron bark gives on mordanted cloth very similar shades to fustic, and the methods of application are essentially the same. Speaking generally, chromium mordants give rather redder shades with quercitron bark; aluminium mordants, paler yellows; and tin mordants, brighter and redder yellows. The extracts and flavin are much more extensively used in dyeing than the bark itself. Bark-extracts are used to a considerable extent in cotton and in woollen printing. Flavin is used principally in wool dyeing either alone or in conjunction with cochineal for oranges and scarlets by the single bath process. Silk is dyed principally with flavin on aluminium mordants with the addition of some tin salt in order to make the shade more brilliant. The bright yellows produced by flavin and quercitron bark are acted upon by light in a similar manner to those dyed with fustic—*i.e.*, they become reddish-brown.

As mentioned under fustic, Tartrazin is far superior as regards fastness to light, although the natural colouring matters are much faster to milling and scouring. A dyestuff fast to light and to milling is Milling yellow O (Cassella).

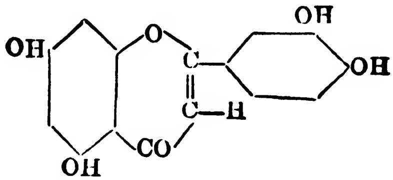
Detection on the Fibre.—The colouring matter of quercitron bark on the fibre gives similar reactions to fustic.

WELD.

Weld is botanically known as *Reseda luteola*, which is a variety of mignonette. It was formerly cultivated in England, and is still grown in France and other parts of the Continent. It is an herbaceous plant, and

grows to a height of about 3 feet. The upper part of the plant, especially the leaves and the seeds, contain the most colouring matter, but the stem is also used in dyeing. Weld comes into the market in the form of sheaves or bundles. It was formerly used to a much greater extent than at present. It has been largely superseded by quercitron bark and flavin. Of late years the greatest amount of weld has been used in dyeing cloth for Government contracts, but Tartrazin and similar yellows are taking its place. The colouring principle of weld is *luteolin*, which was first investigated by Chevreul.

Like morin and quercetin, it is a flavon derivative, its constitution being represented by the formula—



Luteolin forms pale yellow needles. It is very soluble in alcohol, by which solvent it may be readily extracted from the plant. It is only slightly soluble in water, either hot or cold, but dissolves readily in alkalies with a deep yellow colour. Luteolin has been prepared synthetically by St. v. Kostanecki.

Dyeing.—Weld gives with chromium mordants, olive-yellow shades; with alumina, greenish-yellow; with tin, bright yellow; with iron, olive; and with copper mordants, yellow-olive shades. The properties of weld appear to have been overlooked by dyers. It may be considered superior to all natural yellow colouring matters in regard to fastness to light, and is certainly inferior to none as regards fastness to milling. Weld is not much used in cotton dyeing, although, with chromium mordants, it yields a yellowish-olive shade which is very fast to soap and light. For silk it is certainly the best natural yellow, but has been practically superseded by the coal-tar yellows.

The methods of application for weld are practically the same as those for fustic and quercitron bark. Since its colouring power is small, larger quantities of weld are required. It is principally dyed on aluminium mordants, which should be free from iron, since even traces of this metal dull the colour. According to G. H. Hurst, a very bright yellow is obtained with weld on silk mordanted with titanium (see p. 202). The dye-bath is prepared by introducing the requisite amount of weld chopped into small fragments, and enclosed in canvas bags and boiling for about half an hour. The bath should only be prepared as required.

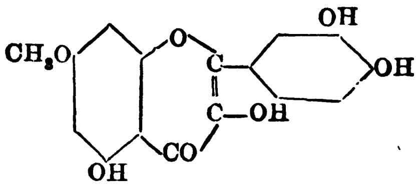
Detection on the Fibre.—The reactions given by weld on the fibre are very similar to those of quercitron bark and fustic. Dyed upon a tin mordant, the fibre is little affected by either dilute acids or alkalies. With stannous chloride and hydrochloric acid the fibre becomes rather redder, whereas fustic and quercitron bark are not appreciably affected. With strong sulphuric acid, the fibre is turned yellowish-olive, and, on addition of water, is almost decolourised.

PERSIAN BERRIES.

Persian berries are the fruit of the buckthorn and of several species of *Rhamnus*, shrubs growing wild and also cultivated in Southern Europe and the East. The product of the *Rhamnus amygdalinus* yields the best quality. The berries are usually gathered before they are quite ripe, which causes them to have a yellowish-green shrivelled appearance. On being kept for a few

years, they become browner, and deteriorate in value, especially if allowed to remain in a damp place. Persian berries possess a disagreeable bitter taste. The colouring principles of Persian berries exist in the form of glucosides. One of these, known as *xanthorhamnin*, may be extracted from the berries by means of alcohol and purified by recrystallisation. It forms golden-yellow needles, soluble in water and alcohol, but insoluble in ether, and is decomposed on boiling with dilute sulphuric acid into *rhamnetin* and a species of sugar. Persian berries also contain the glucosides of quercetin and rhamnazin.

Rhamnetin, to which the constitution



is ascribed, crystallises in microscopic yellow needles. It is only sparingly soluble in water.

Persian berries, like quercitron bark, are used principally in the form of extracts. They are used to a considerable extent in calico-printing for yellow, orange, and green shades. In wool dyeing they have a limited use in conjunction with tin mordants for producing bright yellows and oranges, but, like the other natural yellow colouring matters, the shades turn brown on exposure to light. They are of more use for producing oranges and scarlets with cochineal than for pure yellows; but are more expensive than fustic or quercitron bark, and possess no advantage. Persian berries are also used in woollen printing. Copper mordants give, with Persian berries, a yellowish-olive shade, which is very fast to light. On exposure the shade becomes greener, and actually increases in intensity. Hummel has found that, after exposure for twelve months, such an olive does not fade.

Persian berries dye redder and deeper shades than either fustic or quercitron bark.

Chromium	mordants	give	brown.
Aluminium	,,	,,	bright yellow.
Tin	,,	,,	orange.
Iron	,,	,,	dark olive.
Copper	,,	,,	yellowish-olive.

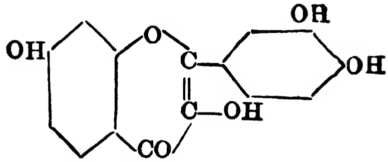
Detection on the Fibre.—The reactions of this colouring matter on the fibre are not sufficiently characteristic to distinguish it readily from quercitron bark. With stannous chloride and hydrochloric acid the fibre becomes yellower, whereas quercitron is not much affected, and weld becomes redder.

YOUNG FUSTIC OR FUSTET.

This dyestuff is the wood of *Rhus cotinus*, a small tree growing in the West Indies and also in the southern parts of Europe. It belongs to the same genus as the sumach tree and is quite distinct from *old fustic*. The colouring principles of young fustic have been investigated by J. Schmidt.* He finds young fustic to contain a substance which is easily broken up by dilute acids or alkalies into a tannin and a glucoside, which, when warmed with dilute sulphuric acid is decomposed into a sugar and fisetin.

* *Journ. Soc. Dyers and Col.*, 1886, p. 148.

Fisetin, having the constitution



crystallises in small lemon-yellow prisms having a composition very similar to quercitrin and closely resembling that compound in its reactions.

Young fustic finds a limited application in dyeing, and yields shades with the various mordants which are very similar to those of quercitron bark. With bichromate of potash the shade is much redder, resembling that given by Persian berries. Young fustic is not so fast to milling or light as any of the other natural yellow colouring matters described, and at the present day it has practically fallen into disuse.

TURMERIC.

Turmeric, also known as Indian saffron, is the underground stem of *Curcuma tinctoria*, a plant growing abundantly in the East Indies and China. The tubers or roots are externally of a greenish-yellow colour, but internally the colour is deep yellow or orange. They possess a strong odour and an aromatic, bitter taste. The roots are ground, yielding a bright orange powder, which should be kept dry; otherwise, if exposed to a damp atmosphere, the colour is deteriorated. Turmeric only yields a small amount of its colouring matter to cold water; hot water extracts a larger quantity, whilst alcohol dissolves it freely.

The colouring principle was isolated by Vogel and Pelletier, who named it *curcumin*. It may be prepared by first extracting the ground root with carbon bisulphide in order to remove the volatile oils and resinous matters. The residue is then treated with dilute caustic soda and the solution acidulated with hydrochloric acid, when the colouring matter is precipitated in yellow flakes. After drying, it may be dissolved in ether and recrystallised. After treating with carbon bisulphide the colouring matter may also be obtained by extracting the residue with dry ether. Pure curcumin, $C_{14}H_{14}O_4$, forms light yellow prismatic crystals which melt at 178° C. It is only slightly soluble in water, but readily soluble in alcohol and ether. It dissolves in alkalies with a deep reddish-brown colour. In this respect turmeric is very sensitive, and paper saturated with a solution of turmeric is frequently used as a test for alkalies. The most characteristic reaction of curcumin and turmeric is with boric acid. If a piece of filter paper stained with a solution of turmeric be moistened with boric acid and dried, it becomes brownish-red; and on now adding a drop of caustic soda it is turned blue or green.

Turmeric is a substantive dye for cotton, wool, and silk, and is used almost entirely in dyeing compound shades. The colour is fugitive to light and is easily affected by soap and weak alkalies. Notwithstanding, large quantities are still used in dyeing cotton, wool, and silk. Although mordants are unnecessary, yet they modify the shade. Bichromate of potash gives a browner shade; alum, a brighter; stannous chloride, bright orange, and ferrous sulphate, olive.

Cotton, wool, and silk are usually dyed with turmeric, without any further addition, or with a little alum, acid, or acid salt. If the bath is in the least

degree alkaline, the fibre is not dyed. It is important that the temperature does not rise much above 60° C., otherwise the shade is both duller and lighter. This is especially the case when no acid is used in the dye-bath.

Detection on the Fibre.—Turmeric gives the following characteristic reactions on the fibre:—

Sulphuric acid,	Fibre and solution reddish-brown; on dilution, fibre pale straw; solution colourless.
Hydrochloric acid,	Fibre reddish-brown; solution, pale pink; on dilution, fibre bright yellow.
Nitric acid,	At first deep-red, then yellow.
Caustic soda,	Bright reddish-orange fibre and solution.
Boiling 5 per cent. solution of sulphuric acid,	Pale yellow solution; fibre paler; red-orange on addition of caustic soda.
Boiling ½ per cent. solution of sodium carbonate,	Orange solution; fibre light brown.
Boiling alcohol,	Yellow solution, green fluorescence.

In a compound shade turmeric may be detected by boiling with alcohol, adding water, and evaporating nearly to dryness with a little wool; and testing the dyed wool as above. Or the alcoholic solution may be concentrated and poured on to a filter paper, and the boric acid test applied as described above.

SAFFLOWER.

This dyestuff consists of the dried flower or head of a kind of thistle, *Carthamus tinctorius*, which is cultivated in Egypt and in some parts of India, and was formerly highly valued on account of the delicate shades of pink which it is capable of producing on bleached cotton. At the present time it is only used in small quantities, its place having been taken by such colours as Erika, the Rhodamines, and Eosines. Two distinct colouring matters have been isolated from safflower—viz., a yellow, soluble in water, amounting, according to Salvétat, to 26 to 30 per cent. of the weight of the dyestuff; and a red or pink, known as *carthamin*, $C_{16}H_{14}O_7$, which is the only valuable constituent, and which, according to the same authority, is only present to the extent of 0·3 to 0·6 per cent. According to L. G. Radcliffe,* who first obtained the colouring matter in a crystallised condition, it is present in the dyestuff in much smaller amount.

Dyeing of Cotton.—The safflower is first macerated with cold water in order to extract the worthless yellow colouring matter. It is then extracted with a weak solution of soda crystals, and in this liquor the cotton to be dyed is worked for some time in the cold. It is then lifted from the bath, which is acidulated with tartaric acid, and, on being returned, the pink colour makes its appearance. In a sense the process is similar to the dyeing of Alkali blue on wool or silk.

Safflower is still used to a limited extent for dyeing red tape. The colour is not fast, being easily discharged by either acids or alkalies, and also by light.

ANNATTO.

This dyestuff is prepared from the fermented fruit of a shrub (*Bixa orellana*), and comes into the market either in the form of an orange-coloured paste or of small seeds which have an orange covering. Its colouring principle, *bixin*, $C_{28}H_{34}O_5$, is practically insoluble in water, but readily soluble in alkalies.

Dyeing of Cotton.—The method is similar to that used for safflower. The cotton is first worked for about a quarter of an hour in a warm (60°) bath,

* *Journ. Soc. Dyers and Col.*, 1897, p. 158.

prepared by extracting the annatto with sodium carbonate. After squeezing, it is transferred to a bath containing dilute sulphuric acid, when the colouring matter develops.

Annatto also finds some application in the tinting of bleached silk, but is now rarely used in dyeing.

THE RED WOODS.

These dyewoods may be divided into two classes—viz., the soft or soluble woods and the hard or insoluble woods, also known as the open and close woods respectively. The colouring matter of the *former* class is easily and freely soluble in water, hence extracts of the woods may be readily prepared. The hard woods, on the contrary, yield their colouring matter but slowly and imperfectly to water.

SOLUBLE RED WOODS.

The soft or soluble class are all obtained from various species of the genus *Cæsalpinia*, belonging to the natural order *Leguminosæ*. The principal varieties are Brazil wood, Peach wood, Sapan wood, Lima wood, and Pernambuco wood. They are imported into this country in the form of crooked and knotty logs, of a dark red colour externally, but nearly colourless in the interior. They possess a slightly aromatic odour and a bitter sweet taste.

Brazil wood is the product of a tree botanically known as *Cæsalpinia brasiliensis*, which grows in the forests of Brazil. It is one of the best of the class, but is now somewhat scarce.

Peach wood, also known as Santa Martha wood, is the product of *Cæsalpinia echinata*, a native of Mexico.

Sapan wood, the product of *Cæsalpinia Sappan*, is imported from Siam, Japan, and East Indies

Lima wood, a variety of sapan or peach wood, is imported from Peru.

All these woods dye very similar shades with the various mordants, and it would appear that they contain one and the same colouring principle. This colouring principle, which is named *brasilin*, does not exist as such in the fresh wood; but is present in the form of a glucoside, a body which, in itself, possesses no dyeing properties. By the action of a peculiar ferment, assisted by a moist atmosphere, the glucoside splits up into brasilein and glucose.

Brasilin was first isolated and studied by Chevreul. It may be obtained from Brazil wood by the method employed for the preparation of hematoxylin from logwood. It possesses the composition $C_{16}H_{14}O_5 + 1\frac{1}{2}H_2O$. The crystals when pure are nearly colourless, and are freely soluble in water, alcohol, and ether. On exposure to air brasilin quickly absorbs oxygen, becoming thereby converted into brasilein. The change takes place more rapidly in the presence of a trace of ammonia. It may be expressed by the following equation:—

$$C_{16}H_{14}O_5 + O = C_{16}H_{12}O_5 + H_2O.$$

This reaction is analogous to the formation of hæmatein by the oxidation of hæmatoxylin. Brasilin, by the action of nitric acid, is partially converted into Picric acid.

Brasilein, $C_{22}O_{16}O_7$, is produced by the oxidation of brasilin, and is obtained as very minute dark crystals, which have a grey metallic lustre; when crushed they give rise to a brown-red powder. It is but slightly soluble in cold, but freely in hot, water; the solution has a pale yellowish-pink colour with a greenish fluorescence.

Application.—Brazil wood and allied woods are used by the dyer both in the form of chips or raspings and extracts of various degrees of strength. At the present day, however, on account of their fugitive character, they are not used to any great extent. They serve chiefly to modify the shades produced mainly by other colouring matters. The woods were formerly used to a considerable extent in calico-printing for producing pinks and purples; but the same shades can be obtained far faster by means of the Alizarin dyes. Crimsons may be obtained by these woods similar in shade to those produced by cochineal, but they are not nearly so fast.

These colouring matters are applied in the dyeing of the various textile fibres in the same manner as logwood.

INSOLUBLE RED WOODS.

The principal woods of this class are saunders-wood, camwood, and barwood. They yield much faster colours than the "open" or soluble class, but the colouring matter is very sparingly soluble in water. On this account extracts are not prepared; the wood itself in a rasped state being used in all cases of dyeing. Although the shades which these woods yield vary somewhat in tone, their properties are so similar, that it is highly probable all contain one and the same colouring principle.

Saunders-wood (known also as *sandal wood*, *santal wood*, and *red sanders*) is the product of *Pterocarpus santalinus*, a tree growing in India, Ceylon, and other tropical parts of Asia, and also in Madagascar. It is imported in logs, which are very hard, compact, and of high density. The exterior is of a dark brown colour, whereas the interior is red. It yields to alcohol about 16 per cent. of an extract which is insoluble in cold, and only very slightly soluble in hot water.

Barwood is the product of *Baphia nitida*, a large tree which grows extensively in Sierra Leone. It yields about 23 per cent. of extract to alcohol. Boiling water extracts about 7 per cent. of colouring matter, but it is almost entirely precipitated on cooling.

Camwood, or kambe wood, is also imported from the west coast of Africa. It yields its colouring matter somewhat more freely than the other two woods. Its price is considerably higher than that of barwood and saunders-wood, but it is considered superior as regards fastness. It gives also brighter and fuller shades.

The colouring principle of saunders-wood, which, as already stated, appears to be identical with that of barwood, is named *santalin*, and is said to have the formula $C_{15}H_{14}O_5$ (or, according to Franchimont, $C_{17}H_{16}O_6$), and is practically insoluble in water.

Application.—Saunders-wood, barwood, and camwood are used principally in wool dyeing, in conjunction with other dyewoods, for producing various compound shades, especially *browns*. The shades obtained are very fast to soaping and milling, and, on that account, are largely used for dyeing heavy woollen cloths, which have to be severely milled. In many cases of wool dyeing, however, these woods have been superseded by Alizarin red and Anthracene brown and the acid chrome colours, which are much faster to light than the red woods. Camwood, saunders-wood, and barwood, especially the latter, are also sometimes employed to give a bottom to woollen cloth which is to be afterwards dyed with indigo. Cudbear is often used for this purpose, but barwood or saunders-wood is much to be preferred.

The shades obtained with these woods vary according to the mordant employed from a dull red to a rich claret-brown. Camwood gives the bluest

and brightest shades; saunders-wood the yellowest shades with the same mordants.

The more important mordants produce the following shades with these red woods:—

Mordant.	Camwood.	Saunders-wood.
Chromium salts, ...	Red-violet.	Brown-red.
Aluminium ,, ...	Red.	Orange-red.
Iron ,, ...	Violet.	Maroon.
Copper ,, ...	Brown.	Brown.
Tin ,, ...	Bluish-red.	Red.

The wool is boiled for one to two hours with 20 to 60 per cent. of barwood or camwood; and afterwards boiled, without washing, in a fresh bath, with 2 per cent. of potassium bichromate, for half an hour. The potassium bichromate may also be added to the dye-bath, but it is preferable to use a fresh bath. In the dyeing of camwood-browns or drabs a certain proportion of logwood and fustic, according to the shade required, is added to the dye-bath. Since the colour is developed in the "bichrome" bath, considerable experience is required to adjust the proper proportions and quantities of woods in order to match a given shade. As the dyeing proceeds, the dyer takes out a small sample of the wool or cloth from time to time and develops it in a small bath of potassium bichromate kept for that purpose. If necessary, a further addition of wood or wood-extract is made to the bath, and the dyeing continued until a small sample develops to the shade required. The bulk is then "saddened" with bichromate of potash, and the goods afterwards washed and dried. Instead of bichromate of potash 5 per cent. ferrous sulphate or copper sulphate may be used as the "saddening" agent.

The red woods in conjunction with other dyewoods are sometimes applied to wool in the following manner:—The goods are mordanted with 2 to 3 per cent. of bichromate of potash, and dyed in a fresh bath with the requisite amount of dyewoods, and then "saddened" with 3 to 5 per cent. of ferrous sulphate.

These colours are very fast to milling, but are more fugitive to light than the anthracene dyes. A shade produced by camwood or saunders-wood, logwood and fustic, appears to be considerably faster to light than that given by any one of these dyewoods alone.

MADDER.

This dyestuff has been used for dyeing and printing from very early times, but since the introduction of artificial Alizarin the amount consumed has decreased almost to vanishing point. It was formerly considered the most important of all dyestuffs used by calico-printers, but it is now entirely displaced in printing by artificial Alizarin.

Madder is the root of a plant known as *Rubia tinctorum*, a native of Asia Minor, but it has long been cultivated in Italy, and later in France and Holland. Madder was known as a dyestuff to the ancient Egyptians, and also to the Greeks and Romans, who fixed it upon cotton much in the same manner as is employed at the present day. The *Rubia tinctorum* is a perennial plant which is commercially propagated by shoots. The herbage is cut off and the roots gathered in the third year: in Turkey and the East, however, it is usual to allow the roots to remain in the ground until the fifth or even the seventh

year. In this manner the colouring matter is slowly developed by the oxidising influences of the air.

The colouring matter resides almost entirely in the cortical part of the root, little or none being found either in the epidermis or in the central woody part. Dutch and Alsatian madder, after being ground, is usually stored in large casks for two or three years, when the colouring matter is further developed and the tinctorial power increased; but if kept much longer than three years, a further change occurs, resulting in a loss of colouring matter. The best madder is obtained from plants grown on calcareous soil.

The principal colouring matters yielded by madder are Alizarin, Purpurin, and Pseudo-purpurin, of which Alizarin is by far the most important. The colouring matter or colouring matters are not contained as such in the fresh madder root, but exist in the form of glucosides, which by the action of a peculiar ferment (also present in the root, and called by Schunck *erythrozym*) split up into colouring matters and sugar.

Rubian or *Ruberythric acid*, the glucoside existing in the fresh madder root, is sparingly soluble in cold water, more easily in hot water, alcohol, and in ether. It dissolves in alkalies with a blood-red colour. When heated it decomposes at 130° C., giving a sublimate of Alizarin. When boiled with dilute acids or by the action of erythrozym (the ferment of madder) it is decomposed into glucose and Alizarin. The change may be represented by the following equation:—

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

Small quantities of other colouring matters are also formed at the same time.

Alizarin, $C_{14}H_8O_4$, is the principal and most valuable colouring matter of madder. It was discovered in 1824 by Robiquet and Collin by treating madder with strong sulphuric acid and gently heating the black mass thus formed.

Alizarin is now manufactured in enormous quantities from anthracene, a body obtained from coal-tar. (See Part VII.)

Purpurin, $C_{14}H_8O_5$, another colouring matter of madder, exists, like Alizarin, in the fresh root in the form of a glucoside. Purpurin resembles Alizarin, but is yellower. It is slightly more soluble in water, communicating to it a pink colour. It dissolves in alkalies with a purple-red colour, which gradually disappears on exposure to the air. The colour of Alizarin is permanent in the air. Purpurin is readily detected in minute quantities, and may be distinguished from Alizarin by means of the spectroscope, or by its solubility in a boiling solution of aluminium sulphate.

Numerous preparations of madder were formerly made; but, since the introduction of artificial Alizarin, they have practically fallen into disuse. The preparations were distinguished as *garancin*, *garanceux*, *fleurs de garance*, "*commercial alizarin*," *madder extracts*, &c.

Dyeing.—With the various mordants madder gives the following series of shades:—

Chromium mordants, . . .	Dull bluish-red to crimson.
Aluminium ,, . . .	Pink to scarlet.
Iron ,, . . .	Maroon to reddish-brown.
Copper ,, . . .	Yellowish-brown.
Tin ,, . . .	Reddish-orange.

The old method of madder dyeing on *cotton* is practically the same as the application of Alizarin (artificial) in Turkey-red dyeing. (See Part VII.)

Madder is used in *wool* dyeing—*e.g.*, for dyeing cloth for the French military uniforms, and in the East for carpet yarn—but otherwise not to any

great extent. It is also used in conjunction with other colouring matters to produce drabs, browns, &c. It is also used by the indigo dyer in the woad vat, but, in this case, madder fulfils the purpose of a ferment rather than a dye. In the dyeing of cotton, madder was formerly a most valuable dyestuff, but, as already stated, it has been practically, entirely, supplanted in Europe and America by artificial Alizarin.

In the dyeing of drabs on *wool*, it is usual to dye and mordant in the same bath, using alum and tartar, and modifying the shade with fustic, logwood, &c., as required. In other cases, madder is applied to wool in a single bath, with the mere addition of a little sulphuric acid. Faster and fuller shades are, however, obtained by the two-bath system, mordanting first and dyeing afterwards. The methods of application are similar to those employed for logwood, &c. In mordanting with bichromate of potash deeper shades are subsequently obtained by adding a third of its weight of sulphuric acid to the bath. By using 60 per cent. of madder a rich brownish-red shade is produced. In dyeing with madder upon wool mordanted with alum, it is often necessary to add acetate of lime in order to obtain the best results. A little sumach added to the bath is beneficial, and brighter shades are obtained at 80° C. than at the boiling temperature. At a lower temperature the yellow colouring matters of madder are not so readily fixed. But in any case the red produced by madder and alum mordant is never as bright as that given by Alizarin.

In the dyeing of *silk*, madder is scarcely ever used.

ORCHIL AND CUDBEAR.

Orchil and cudbear are manufactured from certain genera of *lichens*, small perennial plants belonging to the class *cryptogamia*. These lichens are found growing in the Canary Isles, Cape de Verde Isles, Sardinia, East Indies, Norway, Madagascar, Zanzibar, and various parts of Central and South America. Formerly the whole of the orchil used in Europe was obtained from Florence. The lichens are commercially known as "weeds," and sold under the names of orchella weed, orchil weed, &c. The two principal species growing on the coasts are the *Roccella tinctoria*, known as "Valparaiso weed"; and the *Roccella fuciformia*, sold as "Lima weed," &c. Of the species growing inland, the *Variolaria orcina* of Auvergne and the *Lecanora tartarea* of Sweden are the most important.

Lichens do not contain any colouring matter already formed, but certain colourless compounds, which, by the action of ammonia and the oxygen of the air, are converted into colouring matters. The principal colour-producing compounds existing in the lichens named are erythrin, lecanoric, and evernic acid.

Orchil, or archil, occurs in commerce in two forms—paste and liquor. It was formerly made by treating the lichens with putrid urine, and, at a subsequent stage, with slaked lime. The process usually adopted in England is as follows:—The weed, preferably the *Roccella tinctoria*, is picked, and torn or cut into small fragments, and put into iron drums provided with stirrers and mixed with a dilute solution of ammonia. The temperature of the mass is kept at from 35° to 45° C. for a period ranging from five to six days. A fermentation soon commences, which must be carefully watched and should not be allowed to go on for too long a time; otherwise the colouring matter is destroyed, with the formation of a dirty brown substance. Samples are taken out from time to time and dye-tests made, in order to observe the stage of the operation. When the colouring matter ceases to increase the fermentation is stopped. The product is archil paste. In making orchil *liquor*, the weed is treated with water containing ammonia, and the fibrous matter, which is

practically worthless, removed. The liquid, which contains the colour-giving principles, is then submitted to fermentation, as above described.

Cudbear, which comes into the market in the form of a dark brownish-red or purple powder, is prepared, in the first instance, in the same way as orchil paste. The weed usually selected for cudbear is the *Lecanora tartarea*. When the fermentation is complete the mass is dried and ground.

Orceïn is the principal colouring matter of archil and cudbear. It is produced by the action of ammonia and oxygen on orcinol or orcin, $C_6H_3(CH_3)(OH)_2$. According to Liebermann, two compounds may be produced, depending upon the amount of ammonia used. The composition of the two bodies is given as $C_{14}H_{11}NO_3$ and $C_{14}H_{12}N_2O_3$ respectively.

Dyeing.—Since the introduction of many of the azo-dyes and the application of Alizarin colours to *wool*, the amount of orchil and cudbear used in dyeing has been gradually, though slowly, declining. Nevertheless large quantities of these colouring matters are still used, and, although fugitive, on account of certain characteristics, they seem difficult to replace. Great quantities are used for "bottoming" indigo. Cudbear and orchil are used in conjunction with other dyestuffs for producing compound shades, such as browns, maroons, and clarets, on wool and silk. A considerable amount is used in the dyeing of carpet yarn. The colouring matter is substantive, requiring no mordant, and possesses the useful property of dyeing in a neutral, acid or slightly alkaline bath. It does not rush on to the fibre, but dyes slowly, regularly, and evenly. In deep shades the colour has an intensity and body which cannot be well equalled by any of the numerous coal-tar substitutes. Cudbear and orchil dye best in a neutral bath, producing a bluish-red or dull magenta shade; but they are frequently applied with sulphuric acid in conjunction with extract of indigo and other "acid" colours. An acid bath turns the shade redder and brighter.

About 3 per cent. of sulphuric acid is a convenient amount to use. Frequently alum and tartar are used in place of sulphuric acid. The colour is not fast to light nor milling; but resists soaping fairly well, becoming bluer.

Silk is dyed in a bath containing soap solution with, or without, the addition of acetic acid.

Cudbear and orchil are not applicable to cotton.

Detection on the Fibre.—The ash will probably contain either no mordant or a little alumina. Chromium may be present, especially if logwood, fustic, or similar colouring matter has been used in dyeing the shade. The following reactions are given by the pure colouring matter:—

Hydrochloric acid, .	Solution and fibre red.
Sulphuric acid, .	Fibre and solution purple; on dilution, solution red and fibre almost colourless.
Caustic soda, . .	Fibre and solution bluish-purple, colour slowly removed.
Ammonia, . .	As with caustic soda.
Nitric acid, . .	Yellow.
Stannous chloride, hydrochloric acid, and water,	Decolourised.
Boiling alcohol,	Bluish-red solution.
Boiling carbonate of soda (½ per cent.), .	Violet solution.
Boiling 5 per cent. solution of sulphuric acid, .	Orange solution, turned violet by soda.

In a compound shade, in the presence of indigo, logwood, fustic, alizarin, &c., it is best detected by boiling with alcohol, adding water to the alcoholic extract, and evaporating to a small bulk with a few threads of worsted yarn. The yarn is then dried and carefully tested as above. Orchil and cudbear are thus readily distinguished from Magenta by the action of hydrochloric acid and caustic soda respectively, Magenta being decolourised by both reagents.

COCHINEAL, KERMES, AND LAC-DYE.

These colouring matters are all derived from the animal kingdom.

Cochineal is the female of the *Coccus cacti*, an insect which lives and propagates on certain kinds of cactus, especially the *Nopal* or *Cactus opuntia*. The plant and insect are natives of Mexico and Guatemala, but have been successfully introduced into the Canary Islands, as well as Algeria, Java, and Australia. The production, however, is almost confined to Guatemala and the Canaries. The male insect is much smaller than the female, and is furnished with wings. It does not yield a dye. The female has no wings, and remains attached to one spot on the plant. At the age of about three months the female insects are swept from the leaves into small straw baskets, and are either killed by being thrown into hot water, and afterwards dried in the sun or in stoves; or they are placed in a bag and stoved at once. The latter method yields the silver cochineal, so called on account of the peculiar white lustrous appearance which the product possesses. When the insect is first thrown into water it forms the black cochineal. The weight of the dried insect is about $\frac{1}{10}$ grain, so that 70,000 are required to produce 1 lb. of cochineal. An acre of the cactus yields 250 to 300 lbs. If treated with warm water for some hours the dried insect swells and takes a hemispherical shape, when its structure can be seen.

The colouring principle of cochineal is *carminic acid*, $C_{22}H_{22}O_{13}$ (?).

The aqueous solution of carminic acid is not changed by exposure to the air. It dissolves in caustic alkalies with a beautiful purple colour.

Since the introduction of the azo-scarlets, the amount of cochineal used in dyeing has decreased considerably; nevertheless, it is still used in dyeing woollen cloth, and, to a less extent, worsted yarn and slubbing. The scarlet cloth for the English army is all dyed with cochineal. Formerly a considerable amount of cochineal was used in silk dyeing, but at the present day it has been almost entirely superseded by coal-tar colours. In cotton dyeing cochineal finds little or no application; small quantities are used in the printing of pinks.

In the dyeing of wool, two distinct red shades are obtained by cochineal—viz., a crimson and a scarlet. The latter is of the greater importance, and is obtained by tin mordants. The dyeing and mordanting is done in one bath. A cochineal scarlet is faster to light than most of the artificial reds.. On being scoured or milled it does not lose much colour, but becomes duller and bluer. An azo-scarlet, on the other hand, becomes yellower. A cochineal scarlet does not bleed and stain the neighbouring fibres like the azo-scarlet.

Cochineal gives the following series of shades with the various mordants:—

Chromium mordants,	Purple.
Aluminium ,,	Crimson.
Iron ,,	Purple.
Copper ,,	Claret.
Tin ,,	Scarlet.

Tin and alum salts are the only useful mordants.

Dyeing of Wool.—In dyeing scarlets and oranges with cochineal, the mordanting and dyeing may take place in separate baths or in one bath. The latter is the usual method adopted in practice. When separate baths are used, 4 to 6 per cent. of stannous chloride and a similar quantity of tartar are taken, and the wool entered at about 60° C. The bath is gradually raised to the boil, and kept at or near the boiling point for from three-quarters to one hour. The material is either washed or taken direct to the second bath (containing 10 to 20 per cent. of ground cochineal) and dyed one to one and a

half hours. The shade obtained is a bluish-scarlet. In the one-bath system there are numerous modifications of cochineal-scarlet dyeing. Some dyers use stannous chloride (tin crystals); others tin spirits of various kinds, such as scarlet spirits or nitrate of tin, muriate of tin, sulpho-muriate, &c. The simple chloride of tin, which consists merely of stannous chloride and hydrochloric acid, is, as a rule, to be preferred to the tin crystals, since the free hydrochloric acid, when not present in too great an excess, acts beneficially. The lake formed by the tin salt and the colouring matter of cochineal is kept longer in solution and the colour penetrates to the centre of the cloth, whereas, in the case of hard woollen goods, in the absence of free hydrochloric acid, the colour would be more or less deposited on the surface. Again, in the case of calcareous or alkaline waters, the hydrochloric acid prevents a precipitation and consequent loss of mordant. For 100 lbs. of wool, the dye-bath may be prepared by adding 5 to 6 lbs. of oxalic acid, 4 to 5 lbs. of stannous chloride (or its equivalent of tin spirits), and 10 to 20 lbs. of cochineal. Instead of oxalic acid, tartar or argol, or a mixture of oxalic acid and tartar, may be used. The oxalic acid or tartar should be added to the bath before the stannous chloride, otherwise a precipitation of stannous oxychloride occurs, which not only causes a loss of mordant, but may produce stains. If, however, a solution of stannous chloride containing sufficient hydrochloric acid be used, this precipitation does not take place. After boiling the mixture of dye and mordant for about ten minutes, cold water is added to the bath, and the goods entered at a temperature of about 70° C. The bath is gradually raised to the boiling point during the course of three-quarters of an hour, and boiled for three-quarters of an hour longer. A deficiency of tin gives a dull bluish shade, while an excess produces a paler scarlet. Tartar increases this intensity, and an excess gives a yellower shade of scarlet. As a rule, a small proportion of yellow colouring matter is used in scarlet dyeing, the substances used being weld, flavin, fustic, or Persian berries. For orange shades, of course, larger proportions of yellow and only a small percentage of cochineal are taken. The one-bath system produces yellower and more brilliant shades than when separate baths are used for mordanting and dyeing. More cochineal is required to give a certain shade by the single bath than by the two-bath method, since in the former case much of the colouring matter remains in the bath (after dyeing) in combination with the mordant. For successive lots of material to be dyed, however, smaller quantities of cochineal suffice.

In dyeing with cochineal the vats employed should be either of wood, stone, or metallic tin. In the presence of iron or copper the shades obtained are liable to be dull, since if traces of these metals dissolve they form with cochineal dark violet or purple lakes. If much hydrochloric acid is used the scarlet is not greatly affected by small quantities of iron or copper.

Cochineal crimson is obtained by means of aluminium mordants, and, like the scarlet, may be dyed in either one bath or two. If separate baths are used, the wool is mordanted with 6 per cent. of alum and 6 per cent. of tartar, and dyed in a fresh bath with 15 to 20 per cent. of cochineal. The same proportions may also be used for the single bath method, or oxalic acid may be taken instead of tartar. A bluer shade of crimson is obtained by adding a little alkali to the bath—ammonia or sodium carbonate. The shade may also be modified by adding orchil, cudbear, or ammoniacal cochineal.

Ammoniacal cochineal is obtained by allowing a mixture of ground cochineal and ammonia to remain in contact for some days. The proportions used are one part of cochineal and three parts of ammonia. A chemical change occurs, resulting in the formation of carminamide.

When the change is complete the mixture is heated, in order to drive off the excess of ammonia. In some cases about 40 per cent. of hydrated alumina

is added, and the whole of the ammonia driven off by heat. The mass is afterwards moulded into cakes. Ammoniacal cochineal is used for dyeing wool purple and crimson, and in conjunction with ordinary cochineal for rose reds. The crimsons are not so readily affected by acids as those given by ordinary cochineal. Ammoniacal cochineal gives a beautiful purple precipitate with oxychloride of tin, whereas cochineal itself gives, as previously stated, a scarlet precipitate. The mordant which works best with ammoniacal cochineal is the nitrate of tin.

Rose pink is obtained on wool by dyeing in a vat containing the following ingredients (for 100 lbs.):—2 lbs. of ammoniacal cochineal paste, 2 lbs. of ground cochineal, 1 lb. of tin dissolved in 8 lbs. of nitric acid, and 4 lbs. of tartar. Ammoniacal cochineal also finds some application in the blueing of bleached cotton.

Detection on the Fibre.—The mordant on wool dyed with cochineal will be found to be either tin or alum. The following reactions are given by this colouring matter on wool, mordanted with alum and tin salts respectively:—

Reagent.	Tin Mordant.	Alum Mordant.
Hydrochloric acid, ...	Orange-red.	Scarlet.
Sulphuric acid, ...	Dark violet.	,,
Nitric acid, ...	Yellow.	Yellow.
Stannous chloride, hydrochloric acid and water, ...	Orange.	Orange-red.
Caustic soda, ...	Red-violet.	Red-violet.
Ammonia, ...	,,	,,
Boiling alcohol, ...	*Nil.*	*Nil.*

Cochineal, on the fibre, is distinguished from azo-scarlets by the action of caustic soda; the azo-scarlets being either partially stripped or turned orange, cochineal becoming purple. Boiling weak acids turn cochineal-scarlet yellower, and the solution is reddish-orange, which, on addition of caustic soda, becomes purple. An azo-scarlet is less affected by acids, the solution is a pale bluish-pink, which is either decolourised or becomes yellow-orange on addition of caustic soda. Boiled with a weak solution of soap, cochineal becomes bluish-crimson, azo-scarlets yellower and much lighter. From Alizarin, cochineal is distinguished by the action of weak and strong hydrochloric acid, cochineal being little affected, whereas Alizarin becomes yellow. The acid solution in both cases becomes purple or violet on addition of an alkali.

Kermes consists of the dried insect known as the *Coccus illicis*, which lives on a species of oak, the *Quercus coccifera*. The insects are collected in the month of June, and killed by being exposed to the vapours of acetic acid evolved by heating vinegar. They are afterwards dried, and are then ready for use. Kermes is but little, if at all, used in England; but in South France, Spain, Morocco, and Turkey it is still used for dyeing leather and woollens. Kermes was known to the ancients, and has been used in the East as a dye from time immemorial. The colouring principle of kermes is identical with, or very closely related to, the carminic acid of cochineal. Kermes, as well as cochineal, was formerly supposed to consist of little berries or grains, and the colours dyed with them were said to be grained or ingrained. The term "grain colours" is still used at the present day, signifying shades dyed with cochineal.

Lac-dye is the product of a small insect, the *Coccus lacca*. It is a secondary product in the manufacture of shellac. The insect lives on the twigs of trees of the genus *Ficus*, especially the *Ficus religiosa* or banyan tree, which grows in

Bengal, British Burmah, Assam, and other eastern countries. The insects reproduce and multiply with such rapidity that in a short time they entirely cover the surface of the twigs to a thickness of a quarter of an inch, and adhere very firmly to the wood. The natives break off these twigs just before the time of hatching, and expose them to the sun to kill the insect. The product is stick-lac. It contains about 10 per cent. of colouring matter and 70 per cent. of resin. The stick-lac is ground and triturated for some hours with water, or, according to some authorities, with a weak alkali. The colouring matter dissolves and is precipitated by adding a solution of alum. The deposit is collected and placed on a canvas filter or strainer, and afterwards pressed so as to form cakes about 2½ inches square and from ½ inch to ¾ inch thick. The exact mode of preparation, however, is kept secret.

After treating stick-lac with water, the residue, when dried, constitutes seed-lac. When seed-lac is melted and filtered through cotton it forms shellac.

Lac-dye has been manufactured and used in India for centuries. It was first imported into England in 1796, and at one time was used to a very much greater extent than at present. It produces a colour similar to cochineal, but fuller, although not so brilliant. It is faster than cochineal. This was formerly considered to be due to the presence of resinous matters in lac, but it is more probably a property of the colouring matter itself; since recent investigations have shown that, although similar to carminic acid, the colouring matter of lac is a distinct body, and has been named by Schmidt *laccainic* acid, who ascribes to it the formula $C_{16}H_{12}O_8$.

Laccainic acid forms a brownish-red crystalline powder which melts at 180°. It is soluble in alcohol, wood spirit, and glacial acetic acid.

Lac is used for dyeing wool scarlet, orange, and crimson shades. The colouring matter is only sparingly soluble in water, on account of the presence of so much resinous and mineral matter in commercial lac. Before use, the lac is ground up with the requisite amount of tin spirit, and usually a little hydrochloric acid, and allowed to stand about a day. It is then added to the bath, and the goods are dyed in exactly the same manner as with cochineal, adding either oxalic acid, tartar, or both. In practice, it is often found advantageous to combine the brightness of cochineal with the solidity and permanency of lac dye. Consequently, lac and cochineal are frequently used together; or, after dyeing the wool with lac, it is taken to a fresh bath containing cochineal. A good fast scarlet is produced upon cloth (100 lbs.), by dyeing in a vat containing the following ingredients:—8 lbs. of lac (previously ground up with part of the tin spirits), 5 lbs. of cochineal, 5 lbs. of tartar, 20 lbs. of tin spirit (44° Tw.), and flavin ½ oz.

CATECHU OR CUTCH AND GAMBIER.

These dyestuffs are obtained from various species of *Acacia*, *Areca*, and *Uncaria* growing in India. They closely resemble each other in their properties, and, for some time, there was much doubt regarding their origin. Catechu or cutch, also known as *terra japonica*, is obtained from the softer part of the wood, and from the pods of the *Acacia catechu;* and also from the betel or areca nut, which is the fruit of the palm tree, known as *Areca catechu*. The wood or nuts are boiled in water, and the solution obtained evaporated to a syrup, when it is spread on the ground, and on cooling solidifies.

Catechu has been used in the East from time immemorial for the purposes of dyeing and tanning, and also in medicine.

The two principal varieties of cutch or catechu are known respectively as Bombay and Bengal catechu.

Bombay catechu, the product of *Areca catechu*, is considered to be the best. It is imported in dense irregular lumps of a dark brown colour, weighing about a hundredweight. It dissolves in boiling water with a deep brown colour, and the solution gives copious precipitates with gelatin and sulphuric acid.

Bengal catechu is the product of the *Acacia catechu*. It is of a pale brown colour, and contains less tannin, but more catechin, than the Bombay variety.

Gambier is obtained by extracting the leaves of the *Uncaria gambier*, a shrub growing abundantly in India and the Malacca Islands. Gambier occurs in commerce in blocks and in small cubical pieces. It is opaque and of a brownish-yellow colour. It is only slightly soluble in cold water, but almost completely soluble in boiling water. Its colouring matter is in a less oxidised state than that of cutch.

Catechu or cutch and gambier contain varying amounts of a tannin, known as catechutannic acid or mimotannic acid, and a white crystalline body called catechin or catechuic acid. There is also present a brown amorphous body, produced by the oxidation of the catechin and catechutannic acid during the process of extraction and evaporation.

Catechutannic acid may be prepared by boiling powdered catechu with a small quantity of water, and allowing the mixture to stand some days, in order that the catechin may separate. The solution is filtered and evaporated to dryness. The residue is dissolved in alcohol and the solution treated with ether, and, after again filtering, evaporated to dryness. It may be further purified by treatment with water and ether. Catechutannic acid is readily soluble in water and alcohol, but insoluble in ether. Its aqueous solution gives precipitates with gelatin and with tartar emetic; with ferric acetate it gives a green precipitate. On exposure to air the aqueous solution is gradually oxidised, becoming red. The change takes place very rapidly in the presence of alkalies.

Catechin, $C_{15}H_{14}O_6 + 4H_2O$, may be obtained from the residue after treating catechu with cold water. It is dissolved in a small quantity of boiling water, and precipitated by lead acetate and acetic acid. The precipitate is washed, suspended in water, and decomposed by sulphuretted hydrogen. The filtrate is then carefully evaporated to a small bulk and allowed to crystallise. Catechin may also be extracted from finely-powdered catechu by means of dry ether, in which liquid catechutannic acid is insoluble. Catechin is a white, silky, crystalline body, sparingly soluble in cold water, but freely soluble in boiling water and in alcohol and ether. The aqueous solution gives a green colouration with ferric chloride, but produces no precipitate with gelatin. An alkaline solution of catechin rapidly absorbs oxygen from the air with the formation of a brown substance known as japonic acid. It is said to be this compound which constitutes the brown colour of goods dyed with catechu. Catechu and gambier possess an astringent taste with a sweet after-flavour.

A colouring matter, known in the trade as *prepared cutch* or *patent cutch*, is made from gambier. There are various modes of preparation, some of which are kept rigidly secret. According to one process, the gambier is melted with the addition of about 1 per cent. of bichromate of potash and then poured into wooden frames to solidify. The catechin is thereby oxidised into brown resinous bodies, probably japonic acid and similar compounds. The product dyes much redder shades than the original gambier. In place of bichromate of potash, copper sulphate and alum are sometimes used in the preparation. These substances may be detected in the ash after igniting the sample.

Application.—Catechu and gambier are used largely in cotton dyeing, also in calico printing and in silk dyeing. In the dyeing of wool, these substances

find only a limited application, although they might in many cases be used with advantage. Both the catechutannic acid and the catechin are utilised in dyeing. The former gives olives and brown olives with mordants, and the latter browns of various shades.

Dyeing of Cotton.—There are various modifications of applying catechu and gambier to the textile fibres, and, broadly speaking, the same methods may be used for both wool and cotton. The usual method consists in boiling the cotton with a solution of catechu or gambier with an addition of copper sulphate or copper acetate, in the proportion of one part of copper salt to ten parts of colouring matter. After allowing to stand some hours, the cotton is worked for about half an hour in a fresh bath (hot) containing 2 per cent. of bichromate of potash, washed and dried.

According to the manner in which the dye has been prepared, samples of catechu and gambier behave very differently in the dye-bath. The shade produced by some varieties undergoes but little change when passed into the "bichrome" bath, whilst that of others is developed and intensified greatly. Gambier as a rule develops much more than catechu. If the copper salt is omitted, as it is by some dyers, a greater development takes place in the "bichrome" bath. Copper salts render the shades much faster to light and should always be used in dyeing with catechu. The shades are also considerably deeper. In some cases the copper salt is applied in a separate bath; but the more general plan consists in mixing it with the catechu or cutch, as above stated. The treatment with bichromate of potash is supposed to oxidise the catechin to japonic acid, which, being insoluble, is thus firmly fixed on the fibre. At the same time a certain amount of chromium is fixed on the fibre, so that the latter can be subsequently dyed (or topped) with mordant colours.

Catechu and gambier are largely used in dyeing compound shades in conjunction with logwood, fustic, red woods, &c.

The basic coal-tar colours, such as Bismarck brown, Magenta, Auramine, &c., are frequently employed for topping, the catechutannic acid acting as the mordant for the colouring matter.

Dyeing of Wool.—As already stated, wool may be dyed in the same manner as cotton. Or the wool may be simply boiled in a solution of catechu, and worked in a fresh bath with about 2 per cent. of copper sulphate, ferrous sulphate, or potassium bichromate; the method being essentially the same as that usually employed for camwood browns. From 2 to 5 per cent. give light brown or drab shades; 10 to 20 per cent. good rich browns, which may be modified by the addition of logwood, fustic, &c. In some cases the wool is mordanted with ½ to 1 per cent. before dyeing as well as "saddened" or fixed afterwards in the same manner as fast logwood blacks. Wool dyed with catechu is very fast to milling and scouring and fairly fast to light. If used in large proportions, catechu, however, like other astringents (sumach, myrabolans, &c.), is apt to give the wool a harsh feel. For wool dyeing, if this harshness is found to be a serious obstacle, the cutch should be ground up with cold water, and, after running off the liquor, the residue, consisting mainly of catechin, alone used.

Dyeing of Silk.—Gambier is largely used in black silk dyeing, principally for the purpose of weighting. The silk is first steeped in basic ferric sulphate, and then in yellow prussiate of potash and hydrochloric acid, which thus produces Prussian blue on the fibre. It is then worked in a bath containing about 200 per cent. (for heavy weighting) of gambier; after half an hour 10 per cent. of stannous chloride is added, and the silk is again entered and worked one to two hours. In some cases the addition of stannous chloride is omitted. (See *Black Dyeing of Silk* under *Logwood*, pp. 341 to 347.)

Detection on the Fibre.—Catechu is not often met with on wool, but either upon wool or cotton the ash will usually be found to contain oxide of chromium and frequently copper oxide. The colouring matter is little affected by reagents. The following are its chief characteristics on the fibre :—

Sulphuric acid, ...	Little change; brownish solution.
Hydrochloric acid, . . .	Rather yellower; faint yellow solution.
Nitric acid, ...	Orange.
Caustic soda (10 per cent.), .	Redder.
Boiling 5 per cent. solution of sulphuric acid, .	Fibre yellower; solution light yellow brown; red-brown on addition of soda.
Boiling ½ per cent. solution of sodium carbonate, . .	*Nil.*

PHARMACEUTICS